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TESIS DOCTORAL

Limpieza del PVC plastificado: metodología aplicable a obras de arte y objetos de museo

Cleaning of plasticized PVC: methodology applicable to artworks and museum objects

MEMORIA PARA OPTAR AL GRADO DE DOCTORA

PRESENTADA POR

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Background

The amount of plastic objects found in museum collections is, without exception, growing. It comes as no surprise, that the conservation of plastics is gaining increasing interest and attention. There are many papers published about composition, manufacture and recycling of plastics, but not so much about their degradation, and very few about cleaning and conservation.

During the last years some institutions have developed projects related to plastics cleaning or offered training courses in conservation of modern materials. Some of these institutions are: the ICN, (Netherlands Institute of Cultural Heritage), the Institute for Conservation Sciences of Cologne and the School of Conservation of Copenhagen, in collaboration with the Statens Museum for Kunst or the National Museum of Denmark. Others, like The Getty Conservation Institute or the POPART (Preservation of Plastic ARTefacts in museums) project have been focused on extensive programs and research in plastics cleaning.

On the other hand, surface cleaning is a vital part on the field of active conservation of plastics, requiring a deep knowledge about plastics materials, reactivity and degradation, which is sometimes difficult for conservators and scientists. Therefore, the cleaning of plastics can be considered a very complicated subject to deal with, but interesting and necessary at the same time, becoming a challenge for the conservation world.

Problematic with cleaning plastics

Cleaning always involves: an esthetical point of view (preservation or improvement of the object's appearance), to stop damages and to slow the risk of future physical and chemical alterations, (surfaces become more stable and resistant to degradation).

On the other hand, the plastics in need of cleaning can be in a degradation stage, exhibiting problems such as: deformation, shrinkage, crazing, stress cracking, colour change, surface deposits, brittleness, weakness, softness, and the release of

gaseous breakdown products. Therefore, it is necessary to study how cleaning affects plastics both in good condition and in the active stages of degradation.

Once the need of cleaning has been stablished for a plastic objecy, the next question is "How to clean". Here, the main problem is to know which method can be used for cleaning each kind of plastic without damaging it and to know how this cleaning will affect the material in the future. There is a list of commercial products, (such as cleaning solutions, cloths etc.), used for the cleaning of plastics in the home or in industrial use, but they are rarely specified to a certain type of plastic or fully described in their composition. Therefore, the conservator is left without any real information regarding the risks or effects of using them.

Goals on the research project

Cleaning processes become essential in museum collections due to the necessity of protection against a wide range of particles deposited on the surface. These particles could not only damage the objects but also cause the depreciation of its aesthetic value. Therefore, cleaning treatments seem to be necessary for the preservation of the artistic objects. Since, properties of polymers significantly differ from those of traditional materials, this obliges to look for specific cleaning methods.

Plastics in museums include a large typology of materials. However, this study has been focused on plasticized PVC, which is one of the most used synthetic polymers in the industry and museums collections. Both non-degraded and degraded plasticized PVC surfaces have been investigated in this research.

From the previous reasoning, the following questions were posed as main goals to achieve in the present research:

- Can plastics materials in need of cleaning, especially those in active degradation, be effectively cleaned without causing immediate or long-term damage?

- Can we qualify or quantify the effectiveness of removing typical dirt or degradation products from the surfaces of plastics in art collections?

- Is it possible to evaluate the risk on the cleaning?

In order to solve these questions: a) a methodology for the study of plastics cleaning in museums collections and b) specific guidelines for the cleaning of PVC artefacts in different stages of degradation, have been provided in the present research.

Furthermore, the review of some ethical questions raised by the experimental part has been also included in this research, although they have not been deeply discussed since this is out of the scope of this project.

As cleaning methods, both dry and wet cleaning techniques have been targeted in the present research. While the efficiency and suitability for plasticized PVC objects of the proposed cleaning techniques objects have been assessed. In order to evaluate the efficiency and suitability of the cleaning objects, several examination and analytical techniques have been proposed, such as: SEM, Optical Microscopy, GC-MS, ATR-FTIR, SEM, Profilometry of non contact, Gloss Measurement and Colorimetry. Other techniques like XPS or XRF have been uses assecundary techniques to assess the cleaning effects and efficiency.

In the experimental part, both a commercial plasticized PVC and an old doll made of plasticized PVC and showing degradation signs have served as study material, in order to evaluate real cases for conservators and researchers, when cleaning plasticized PVC objects in museums and art collections. Furthermore, samples from the commercial plasticized PVC were aged and analysed before and after the cleaning treatments. In this way it was possible to know the effects on "old" or "degraded" samples, which is closer to real objects in museums collections.

Antecedentes

La cantidad de objetos de plástico que se encuentra en las colecciones de los museos es, sin lugar a dudas, cada vez mayor. Por ello, no es de sorprender que la conservación de los objetos realizados en materiales plásticos esté ganando cada vez mayor interés y atención. Existen numerosos artículos publicados acerca de la composición, fabricación y reciclado de plásticos, pero no tanto sobre su degradación, y muy pocos sobre su limpieza y conservación.

Durante los últimos años, algunas instituciones han desarrollado proyectos relacionados con la limpieza de plásticos o cursos de formación sobre la conservación de materiales modernos. Algunas de estas instituciones son: el ICN, ("Netherlands Institute of Cultural Heritage"), el "Institute for Conservation Sciences of Cologne" y la "School of Conservation of Copenhagen", esta última en colaboración con el "Statens Museum for Kunst" o el "Nacional Museum of Denmark". Otros, como el Getty Conservation Institute o el proyecto POPART (Preservation of Plastic ARTefacts in museums) se han centrado en extensos programas e investigaciones sobre la limpieza de plásticos.

Por otra parte, la limpieza de la superficie es una parte fundamental en el campo de la conservación activa de los materiales plásticos, lo que requiere un profundo conocimiento de dichos materiales, su reactividad y degradación, resultando en muchos casos difícil para conservadores y científicos. Por tanto, la limpieza de plásticos puede considerarse un tema complejo, pero al mismo tiempo interesante y necesario, lo que lo convierte en un desafío dentro del mundo de la conservación.

Problemática con la limpieza de plásticos

El proceso de limpieza implica siempre: un punto de vista estético (conservación o mejora de la apariencia del objeto), parar los daños, y disminuir el riesgo de futuras alteraciones físicas y químicas, ya que las superficies se vuelven más estables y resistentes a la degradación. Por otro lado, los plásticos con necesidad de limpieza pueden encontrarse en estado de degradación, exhibiendo

problemas tales como: deformación, contracción, agrietamiento, fisuras, cambios de color, depósitos superficiales, fragilidad, debilidad, reblandecimiento o emisión de productos de degradación en estado gaseoso. Por lo tanto, el estudio de los efectos dela limpieza sobre materiales plásticos debe investigarse tanto en superficies en buenas condiciones de conservación, como en aquellas que se encuentran en las fases activas de la degradación.

Objetivos del proyecto de investigación

Los procesos de limpieza son esenciales en las colecciones de los museos, debido a la necesidad de protección frente a una amplia gama de partículas depositadas en la superficie. Estas partículas no sólo pueden dañar los objetos, sino que también pueden hacer que se deprecie su valor estético. Por tanto, parece evidente la necesidad de los tratamientos de limpieza para la conservación de los objetos artísticos.

Las propiedades de los polímeros difieren significativamente de las de los materiales tradicionales, lo que obliga a la búsqueda de métodos de limpieza específicos. Si bien la variedad de plásticos que pueden encontrarse en museos abarca una gran tipología de materiales, el presente trabajo se ha centrado en PVC plastificado, ya que es uno de los polímeros sintéticos más utilizados en la industria, así como es notablemente presente en museos y colecciones de arte. Para ello, se han incluido en la investigación tanto superficies de PVC plastificado no degradadas como degradadas.

Dado lo anteriormente expuesto, las siguientes preguntas han sido planteadas como objetivos principales a alcanzar en la presente investigación:

- ¿Pueden los materiales plásticos en necesidad de limpieza, especialmente los de la degradación activa, ser limpiados con eficacia sin causar daños inmediatos o largo plazo?

- ¿Podemos calificar o cuantificar la eficacia de la eliminación de suciedad o de productos de degradación de las superficies de plástico presentes en las colecciones de arte?

- ¿Es posible evaluar el riesgo de la limpieza?

Para resolver estas preguntas: a) se ha propuesto una metodología de estudio de la limpieza de los objetos plásticos en los museos y colecciones y b) se han elaborado directrices específicas para la limpieza de artefactos de PVC en diferentes etapas de la degradación.

Por otra parte, la revisión de algunas cuestiones éticas planteadas durante la parte experimental han sido incluidas en esta investigación, aunque no han sido discutidas en profundidad por no ser parte del objeto de este proyecto.

Como métodos de limpieza, tanto técnicas en seco como en húmedo han sido examinadas en el presente trabajo, así como han sido evaluadas la eficacia y la idoneidad de las técnicas propuestas para la limpieza de PVC, utilizando diferentes métodos de examen y técnicas analíticas, tales como: SEM, microscopía óptica, GC-MS, ATR-FTIR, Profilometría de no contacto, medición del brillo y colorimetría. Otras técnicas como XPS o XRF han sido utilizadas como métodos secundarios en la evaluación de los efectos y eficiencia de las limpiezas.

En la parte experimental, PVC plastificado comercial y una muñeca antigua de PVC plastificado con signos de degradación han servido como material de estudio, con el fin de evaluar casos reales a los que se enfrentan conservadores e investigadores cuando deben limpiar objetos de PVC plastificado en museos y colecciones de arte.

Por otra parte, muestras provenientes del PVC plastificado comercial fueron "envejecidas" y analizadas antes y después de los tratamientos de limpieza. De este modo, pudo evaluarse los efectos sobre muestras "envejecidas" o "degradadas", lo que puede considerarse más realista respecto a los objetos que se encuentran en las colecciones de los museos.

1. INTRODUCTION

1.1. Polymers

From a general point of view, "plastics materials, before compounding with additives, consist of a mass of very large molecules. In the case of a few naturally occurring materials, such as bitumen, shellac and amber, the compositions are heterogeneous and complex but in all other cases the plastics materials belong to a chemical family referred to as high polymers" (Brydson, 1999). Thus, plastics are related to *Polymers*, but what is a polymer? Etymologically speaking, the word *Polymer* comes from Ancient Greek and means "many-parts". Under certain conditions the combination of smaller parts, named *Monomers,* forms the polymer molecule itself, which can have different sizes, depending on the number of monomers or the degree of polymerization (Chanda and Roy, 1998). Whilst all plastics are polymers, not all polymers are plastics. Polymers include plastics and rubbers, as well as many natural polymeric compounds.

Generally there are three physical states or states of aggregation: solid, liquid and gaseous. Simple molecules can change from one physical state to another at a fixed temperature, which varies according to the substance. Amongst polymers, however, changes of state are less well defined and may occur over a finite temperature range (Brydson, 1999). According to their macromolecular structure and temperature-dependent physical properties, polymers are divided into three main categories: *thermoplastics, elastomers* and *thermosets*. Unlike the first category, which refers to polymers that can be heated and remodelled, elastomers and thermosets do not change with temperature once they have been formed or manufactured. Nevertheless, elastomers and thermosets differ in elasticity, since elastomers are soft and thermosets are not.

On the other hand, if looking at the chemical structure and the degree of crosslinking within the molecules, thermoplastics, elastomers and thermosets have very different characteristics. As shown in Figure 1 (Menges, 1996), thermoplastic structures can be either linear or branched with no crosslinking within the macromolecular chains, while elastomer and thermoset macromolecules have side chains with complex structures: from low crosslinking in the case of elastomers to high crosslinking in thermosets. In thermoplastics, the macromolecular structure is given by the chemical structure of the monomer units, the order of the monomer units in the molecular chain and the existing side chains (Klein, 2011). Depending on the order of the molecules in the polymer, thermoplastics are divided into two groups: amorphous (where the polymer´s chains are randomly distributed) and crystalline (where a certain degree of order exists amidst the polymer´s chains).

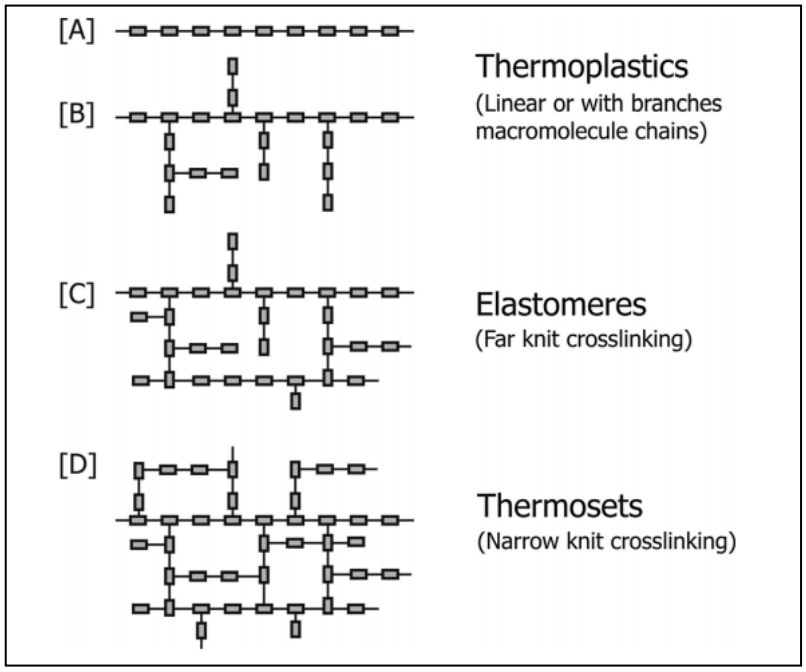


Figure 1. Polymer Types and Structure.

The polymers used in modern plastics are mainly synthetic. Nevertheless, natural polymers, synthesized by living organisms also exist and have been used since ancient times, for example bitumen, horn, ivory, tortoiseshell, cellulose or casein (García Fernández-Villa, 2010).

From a conceptual point of view, "plastics" are versatile materials that can be modelled into a large range of shapes and textures and have been employed as substitutes of other materials (like ivory, wood etc.) or in combination with other materials, such as blends of wood and resins, polyesters reinforced with glass fibres etc. A wide variety of plastic objects extensively present in our daily life (i.e. furniture, toys, cutlery etc.) are now found in museums and art collections as memories of our recent past (Figure 2) (Mills, 2005). In other cases, artists make use of new or recycled plastics materials for the creation of artwork because through these materials they can express their feelings and emotions.

Figure 2. Zoe Leonard "Mouth open, teeth showing", 2000. Reproduced with permission from William and Ruth True collection.

Looking back into history, it was not until the twentieth century that phenolics became the first commercially successful fully synthetic resin and celluloid became the first plastic material obtained by the chemical modification of a polymer (Brydson, 1999). Semi-synthetic and synthetic polymers were initially created and used to imitate expensive and scarce natural materials, such as ivory or tortoiseshell, which were not affordable for the majority of the population. In this way, "luxurious materials" could be artificially synthesized and made more widely available for consumers. One such material is cellulose acetate, a cotton-based synthetic plastic that was marketed as *Secoidin* during the early twentieth century. Another important solid plastic was Bakelite (a phenol formaldehyde resin), discovered by Belgian chemist Leo Backeland (Quye and Williamson, 1999) and introduced into popular use

in the 1920s. During the 1930s and the 1940s, plastics started to be developed and, during these decades, four of today's major thermoplastics were synthesized: polystyrene (PS), polyvinylchloride (PVC), the polyolefins (e.g. polypropylene (PP) or polyestyrene (PE)) and polymethyl methacrylate (PMMA) (Brydson, 1999). In the 1950s, plastics were manufactured as fibres contributing to the development of new textiles. Also toys and domestic objects were manufactured with plastics material, getting introduced as daily life objects. In the 1960s and 1970s, plastics started to be used to as part of furniture, varnishes and paints, like water based acrylic paints. From the 1980s until now, the diversity of plastics has continuously grown, being developed as high performance materials used in medical devices, the aerospace industry, the nano and biotechnology, etc.

In both cases, conceptually and historically, due to their comparatively recent discovery and development, plastics only constitute the raw material for relatively modern artefacts, a minor, though increasingly important part of museum collections (Mills and White, 1994).

1.2. Polyvinyl Chloride (PVC)

Polyvinyl chloride, (IUPAC Polychloroethene) commonly abbreviated as PVC, is a widely used thermoplastic polymer that was accidentally discovered in the ninetieth century by two researchers: the French physicist and chemist Henri Victor Regnault in 1838 and the German Eugen Baumann in 1872. However, it was not until 1913 when the German chemist working at IG Farbenindustrie AG, Friedrich Heinrich August Klatte, patented a a process for the polymerization of PVC for fibre production (Patent DRP 281.877, 1913). It was based on the addition of peroxide directly to the monomer and completing the hardening of the polymer using sunlight. Nonetheless, the material remained to be no more than a scientific curiosity for more than a decade, since the fibres were of very poor quality and the pure PVC is unmanageable and thermally unstable.

1.2.1. Industrial development and presence in art collections

Commercial interest in polyvinyl chloride was revealed in a number of patents independently filed in 1928 by the Carbide and Carbon Chemical Corporation, Du Pont and IG Farben (Brydson, 1999), but the most significant breakthrough occurred in the United States, when the company B.F. Goodrich hired the industrial scientist Waldo Semon to develop a synthetic replacement for the increasingly costly natural rubber. He discovered that the properties of PVC could be modified when polymerised with a number of solvents such as chloronaphthalene, o-nitrondiphenylether, tricresyl phosphate, benzyl benzoate or dibutyl phthalate (Semon, 1932; Semon, 1937), yielding a stiff, rubber like product after cooling. The addition of these "plasticisers" now yielded a material that could be processed at acceptable melt temperatures into products which were permanently soft and flexible. During the same time the first heat stabilizers started to be used in PVC compositions (Leadbitter *et al.*, 1994). Through the 1950's many more companies started to make PVC and the production volumes of this polymer increased dramatically around the world during the 20th century, until becoming the second most important polymer worldwide (Menges, 1996) (Figure 3).

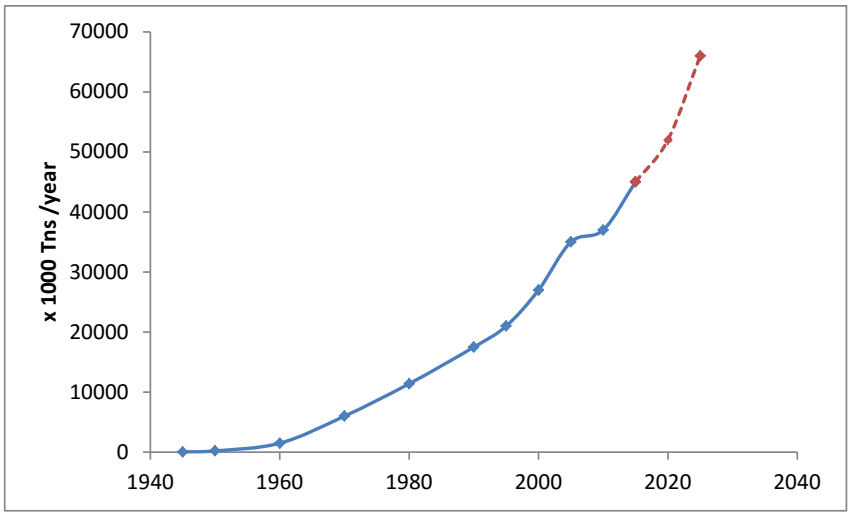


Figure 3. Worldwide annual PVC consumption since 1945 and prevision for future.

As a particular characteristic, PVC is one of the few polymers that are insoluble in their monomer, which gives the possibility to control morphology during polymerization by using surfactants at the polymer/monomer interface. Regarding the chain-growth polymerization of PVC, there are three major types designed to produce vinyl resin of different particle size and morphology: *suspension*, *emulsion* and *bulk* (Kutz, 2011). The suspension process is currently dominating industrial PVC production, accounting for about 75% of the world´s PVC capacity (Mishra and Yagci, 1998).

During the suspension polymerization process, high levels of agitation and dispersant chemicals are employed to suspend drops of vinyl chloride monomer (VCM) in water during the polymerization. This produces a slurry of PVC grains in water having an average grain size, generally between 120 and 150 microns. The process consists of four basic steps: polymerization, stripping to remove residual VCM, centrifugation to remove water and drying (Wilkes *et al.*, 2005). Alternatively, emulsion polymerization and bulk polymerisation are technologies less extensively employed to manufacture PVC. The emulsion polymerization is used to produce specialty resins for paste applications (Mishra and Yagci, 1998), yielding a powder of small particle size with very few free monomer. Bulk polymerization produces a PVC quite similar to the one obtained by the suspension process, but with more porosity of the particles. Both techniques comprise only a small fraction of the global PVC production (Kutz, 2011). Vinyl chloride polymer or copolymer may be also combined with other raw materials to form a "composition" or "compound", being plasticizers the most significant additives in PVC.

In the industry, PVC has been widely used for many different types of applications such as building and construction, cables, the automotive industry, electrical appliances, medical devices, packaging, etc. From a quantitative point of view, the major uses of PVC are in pipe and fittings (35%), films and sheets (15%), flooring materials (10%), wire and cable insulations (5%), automotive parts (5%) and adhesives and coatings (5%) (Chanda and Roy, 1988).

Despite the significance of PVC in the industry, its role as material used in art and design should be also taken into account. As many other plastics, PVC provides the creation process with a freedom not offered by traditional materials like stones or ceramic, which has enabled designers to change the course of fashion design (Quye and Williamson, 1999). As a result, "iconic PVC objects" can be found in museums and art collections like examples of pieces that were created as ordinary objects, but whose success made them unique and timeless. For instance, the worldwide reknown "Blow Chair" from designers De Pas, D'Urbino, Lomazzi and Scolari (Figure 4) is nowadays part of contemporary art collections such as the MOMA (New York) and the Victoria and Albert Museum (London). From the ninetieth century, artists have used PVC material for the creation of art objects such as the artwork "Flag", made by the Danish artist Peter Louis-Jensen in 1969 (Lundbye and Cone, 2013) or the recently restored "Aeromodeller 00-PL" (1969-1971), made by the Belgian artist Paramarenko, which has become a paradigm of PVC in art (Huys and van Oosten, 2005).

Figure 4: Chair "Blow", 1967. Designers: De Pas, D'Urbino, Lomazzi and Scolari. Photograph courtesy of Zanotta spa (Italy).

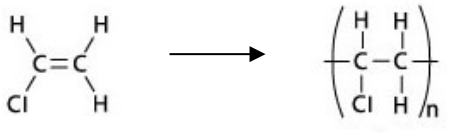
Furthermore, PVC material has been used not only for the creation of imaginative objects, but also for the performance of complex installations where the visitors are intended to directly interact with the artwork (Figure 5). Therefore, it can be stated that PVC forms part of our cultural heritage, either as objects coming from our recent past or as the most actual artistic creations.

Figure 5: Victorine Müller: "Ballon Stratosphérique".
Photograph courtesy of the artist.

1.2.2. Chemical, physical and mechanical properties.

Polyvinylchloride (PVC) is a thermoplastic polymer made up of 58 wt% chlorine plus 42 wt% hydrocarbon (Wilkes *et al.*, 2005). PVC, which is often supplied as a powder, is blended with a high diversity of compounds such as additives, pigments, plasticizers etc. For its modern industrial production, the first educt chlorine is produced by electrolysis of brine, while the second, ethylene, yields from steam cracking in petrochemical processes (Leadbitter *et al.*, 1994). Ethylene is then chlorinated, either by direct or oxychlorination, the resulting ethylene dichloride is then thermally cracked to gaseous VCM (vinyl Chloride monomer): CH_2=CHCl.

Polyvinyl chlorine is obtained from the polymerisation of the monomer vinyl chloride by free-radical mechanisms (Leadbitter *et al.*, 1994) at temperatures generally between 40 and 70ºC (Kutz, 2011):



Monomer Polymer

As PVC is insoluble in vinyl chloride monomer, the polymerization is a heterogeneous process. The polymer phase separates from the monomer phase at conversion of 0.1% and the polymerization occurs in both the monomer phase and the polymer phase. The volume of the monomer phase decreases as the polymer phase grows and absorbs the monomer. At a higher conversion the monomer in the polymer-rich phase continues to polymerize (Mishra and Yagci, 1998).

According to the ease of the homolytic splitting of the π bond in the monomer, radical polymerization takes place in the presence of suitable initiation systems. For the production of free radicals available for the polymerization of VCM, three methods are commonly used: a) thermal cleavage of azo or peroxo compounds (e.g. dioctanoyl peroxide and dicetyl peroxydicarbonate), b) oxidation-reduction processes and c) metal alkyls in connection with oxygen (Kricheldorf *et al.*, 2004).

The free radical polymerization of vinyl monomers includes chain initiation, propagation, chain transfer to monomer and bimolecular termination reactions. However, there is strong evidence that, in free-radical polymerization of VCM some reactions involve complex kinetic mechanisms (Asua, 2007) as shown in the following sequence (Mishra and Yagci, 1998):

Initiation	$I \longrightarrow 2R^{\bullet}$
Propagation	
Head-to-tail propagation	$P^{\bullet}_{n} + M \longrightarrow P^{\bullet}_{n+1}$
Head-to-head propagation	$P^{\bullet}_{n} + M \longrightarrow P^{*}_{n+1}$
Chlorine shift reaction	$P^{*}_{n} \longrightarrow (P^{*}_{n})'$
Tail-to-tail propagation	$P^{*}_{n} + M \longrightarrow P^{\bullet}_{n+1}$
Formation of chloromethyl branches	$(P^{*}_{n})' + M \longrightarrow P^{\bullet}_{n+1}$
Splitting off chlorine radical	$(P^{*}_{n})' \longrightarrow M_n + Cl^{\bullet}$
Initiation of polymer radicals by chlorine radicals	$Cl^{\bullet} + M \longrightarrow P^{\bullet}_{1}$
Chlorine radical transfer to polymer	$P^{\bullet}_{n} + Cl^{\bullet} \longrightarrow P'_{n} + HCl$
Propagation toward formation of a chain branch	$P^{\bullet}_{n} + M \longrightarrow P^{\bullet}_{n+1}$
Formation of an internal double bond	$P^{\bullet}_{n} + M \longrightarrow Cl^{\bullet}$
Chain transfer to polymer	$P^{\bullet}_{n} + M_m \longrightarrow M^{\bullet}_{n} + P^{\bullet}_{m}$
Formation of long-chain branch	$P^{\bullet}_{n} + M \longrightarrow P_{n+1}$
Termination	
Combination	$P^{\bullet}_{n} + P^{\bullet}_{m} \longrightarrow M_{n+m}$
Disproportionation	$P^{\bullet}_{n} + P^{\bullet}_{m} \longrightarrow M_n + M_m$
Primary radical termination	$P^{\bullet}_{n} + R^{\bullet} \longrightarrow M_n$
Termination with $Cl^{\bullet}$	$P^{\bullet}_{n} + Cl^{\bullet} \longrightarrow M_n$

In general, about 1000 monomer units comprise a PVC chain, which is usually formed by head-to-tail addition. The chain growth takes place rapidly and the final step is the termination of chain growth mostly by radical transfer reaction to monomer. The monomer radical is able to start a new chain (Kricheldorf *et al.*, 2004). However, when head–to-head addition occurs, the unstable end of the growing chain rearranges to yield a terminal double bond and a chloride atom (Figure 6). Since the chloride atom is a free radical, it starts the polymerization of

another chain (Kutz, 2011). Chain transfer and control of molecular weight are mediated by the activation energy of head-to-head addition, and thus by polymerization alone, what makes PVC the only major commercial polymer where polymerization temperature controls molecular weight and molecular weight distribution (Kutz, 2011).

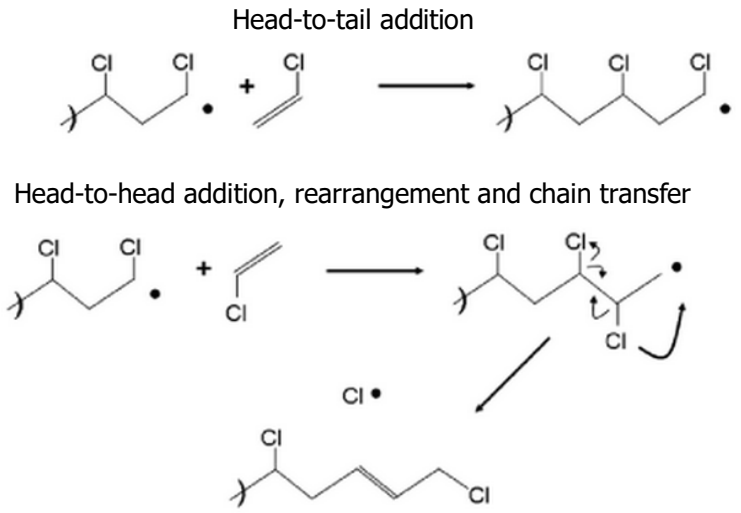


Figure 6: Addition of VCM to growing PVC chain.

Regarding its inner chemical structure, poly vinyl chloride contains three basic types of bonds: C-C, C-H and C-Cl, whose average properties are shown in Table 1 (Wypych, 2008).

Table 1: Average properties of PVC bonds.

Bond	Bond length, pm	Bond radius, pm	Bond dipole moment, Debye
C-C	154	77	0
C-H	109	3	0.40
C-Cl	177	99	1.46

PVC resins show a random distribution of molecular weights and consequently, numerical values are expressed in terms of average. Depending on the application,

PVC molecular weight (Mw) ranges from 39.000, used for injection moulding of thin-walled parts, to 168.000, used for plasticized PVC (Wilkes *et al.*, 2005). In addition, particles of PVC polymers cover a wide range of sizes as shown in Table 2 (Leadbitter *et al.*, 1994).

Table 2: Typical Particle Sizes of PVC.

Polymer	Typical Mean Size (microns)	Range (microns)
Unseeded emulsion latex	0.1	0.01-0.2
Seeded emulsion latex	1.0	0.1-3.0
Microsuspension latex	1.0	0.2-2.0
Emulsion polymer	40-50	0.1-100
Mass polymer	100-150	80-200
Suspension polymer	100-150	50-250

As a polymer, polyvinyl chloride is linear and substantially thermoplastic, where the presence of the chlorine atom causes an increase in the inter chain attraction and hence an increase in the hardness and stiffness of the polymer. Furthermore, the chlorine atoms on the hydrocarbon chain leads to high polar secondary valence forces, which are responsible for the relatively high freezing temperature of 80 to 90ºC (Menges, 1996).

The crystallinity extend of polymers depends on the structure and the secondary bonds within the molecule: the greater the structural regularity and symmetry of the polymer molecules and the stronger the secondary forces, the greater the tendency towards crystallization (Chanda and Roy, 2006). By means of X-ray studies it has been verified that vinyl chloride polymer (as normally prepared in commercial processes) is substantially amorphous, although some small amount of crystallinity (about 5% as measured by X-ray diffraction methods) is present (Brydson, 1999). The degree of crystallinity affects many properties, such as density, antiplasticization, fusion, tensile strength and elongation. Furthermore, crystallinity is related to the physical ageing, since the quality of crystallites influences the structure

of the amorphous phase, which is responsible for the ageing phenomena (Wypych, 2008).

Crystallinity in bulk polymers can be classified as "extended chain and folded chain". In polymers chain folding, the polymer chains can fold in a regular fashion to form plate-like crystallites called lamellae, while extended chain crystallinity arises in many polymers with highly regular structures (Mitchell, 2004). Polymers such as polyvinyls, polyamides and polyesters are much easier to crystallize than the cross-linked or branched polymers, although they cannot be crystallized 100% and they become semicrystalline polymers. The arrangement of chains in crystalline regions is believed to be due to a combination of folded and extended chains (Bronzino, 2006).

The stereochemical order of the substituents groups on a polymer chain (tacticity) can give three distinct structures: *isotactic*, when all the groups are on the same side of the polymer chain; *syndiotactic,* when groups are alternatively distributed in the polymer chain and *atactic*, where the groups are randomly distributed in the polymer chain. Vinyl polymers (-CH_2-CHX-) can have the three possible arrangements of side groups (X): atactic, isotactic and syndiotactic. If side groups are small and the chains are linear, the polymer crystallizes easily. The isotactic and syndiotactic polymers usually crystallize even when the side groups are large (Bronzino, 2006).

Because vinyl chloride is not a symmetric molecule it could have explicit tacticity. However, PVC does not have regular tacticity in practice, because the growing end of the chain is a free radical at a sp^2 hybridized carbon centre that can freely rotate. This rotation rate increases with temperature. Thus, a more syndiotactic polymer can be obtained by polymerizing vinyl chloride at very low temperatures (Kutz, 2011). Studies using NMR techniques indicate that conventional PVC is about 55% syndiotactic and the rest largely atactic in structure (Brydson, 1999). In PVC, the side groups are large (Cl) and randomly distributed along the chain (atactic), then a non-crystalline struture is formed. Due to the relative polarity

of the PVC, only polar liquids can penetrate and dissolve it (Menges, 1996). Also, it has been suggested that PVC is capable of acting as a weak proton donor and thus effective solvents are weak proton acceptors (Brydson, 1999). Furthermore, crystalline and amorphous regions can be detected by means of IR spectroscopy in the PVC polymer, as well as the change in the crystallinity can be quantified by measuring the ratio of specific peaks in the PVC polymer (i.e. CH_2 bands at 1426 cm^{-1} and 1435cm^{-1} represent amorphous and crystalline regions respectively) (Denizligil and Schnabel, 1994).

Other physical properties of PVC for instance are its low combustibility, due to its high halogen content (57%), its ductility and toughness (Lampman, 2003). As a summary, some of the main physical and mechanical properties of PVC polymer are shown on Table 3 (Brydson, 1999; Wilkes *et al.*, 2005; Chanda and Roy, 2006; Klein, 2011).

Table 3: Some Physical properties of PVC polymer

Property	**Value**	**Unit**
Density	1.35-1.45	g/cm^3
Thermal Coefficient of Expansion	80	$K^{-1} \times 10^{-6}$
Young's Modulus (Stiffness)	2.5-4.1	10^3 MPa
Temperature of use	-15-60	^oC
Specific weight	1.38 – 1.24	g/cm^3
Tensile Strength	40-60	N/mm^2
Glass Transition Temperature (T_g)	81	^oC
Crystalline Melting Temperature (T_m)	212	^oC
Brittleness Temperature	> 23	^oC

1.2.3. Plasticizers and additives

PVC polymer is a rigid colourless material with limited heat stability (Brydson, 1999) that rapidly degrades at temperatures required for processing (Leadbitter *et al.*, 1994). In order to make it suitable for use, compounds that change its properties

have to be added. A wide range of products can be obtained from PVC by means of additives such as plasticizers, UV and heat stabilizers, lubricants, and fillers. Other miscellaneous materials occasionally used are fire retardants, impact modifiers or UV absorbers and antioxidants (Table 4) (Leadbitter *et al.*, 1994; Chanda and Roy, 1998; Brydson, 1999; Titow, 1984).

Table 4: Additives of PVC polymer.

PVC Additives
Stabilisers: Lead compounds, organotin compounds, CaZn stabilisers etc.
Plasticizers: Phthalic acid esters, phosphoric acid esters etc.
Lubricants: Stearic acid, paraffin wax etc.
Impact Modifiers: Toughening agents, e.g. ABS (acetonitrile butadiene styrene), MBS (methacrylate butadiene styrene), EVA (ethylene-vinyl acetate copolymer), ACE (acrylate polymethacrylate copolymer) etc.
Fillers: Calcium carbonate, china clay, talc etc.
Fire retardants/smoke suppressants: Aluminium trihydrate, zinc borate etc.
Colorants: Pigments and dyestuffs.
Antistatic Agents: Phosphorous and sulphur compounds.
Biostabilisers: OBPA, (10,10-oxybisphenoxarsine), 8-quinolinolate, N-(trichloromethylthio)phthalimide, zinc pyrithione, etc.
Antioxidants/UV Absorbers: Benzotriazoles, zinc oxide, titanium dioxide etc.

Among PVC additives, the majority compounds in flexible PVC are **plasticizers**. In terms of uses, about the 30% of the total PVC resin production in Europe is used for flexible products (PVC Organization, http://www.pvc.org/en/p/what-is-pvc). Thus, in order to distinguish between rigid and flexible PVC, IUPAC has adopted the nomenclature PVC-P, for plasticized PVC, and PVC-U for unplasticized polymer (Leadbitter *et al.*, 1994; Kricheldorf *et al.*, 2004; Wilson, 1995). Plasticizers, defined as "substances incorporated into a material to increase its flexibility, softness, distensibility or workability", are typically high boiling, oily, organic liquids (Wilson, 1995).

Due to polyvinyl chloride's glass transition temperature (T_g) of 83ºC degrees, PVC polymer makes behaves as a brittle solid at room temperature. Adding a small amount of plasticizer to PVC can lower the T_g to minus 40ºC degrees), making PVC flexible (Wilkes *et al.*, 2005) and usable for manufacturing a wide range of products. However, by adding plasticizers, not only T_g is diminished, but also the crystallinity of the PVC polymer, the tensile strength and the chemical resistance decrease, which is clearly a drawback (Chanda and Roy, 2006). In addition, some properties of PVC such as hardness, tensile strength, ultimate elongation, flexibility, low temperature modulus and brittleness, are influenced by plasticizers level and type (Wilkes *et al.*, 2005). This means, that changes in the proportion and nature of the plasticizer in the PVC composition affect the physical and mechanical behaviour of the polymer.

From a physical point of view, plasticized PVC has the classic morphology of a TPE (Thermoplastic Elastomer) and has stable and meltable physical cross-links consisting of PVC crystallites (Figure 7, Wilkes *et al.*, 2005), which survives in the presence of plasticizer to about 160ºC and above. In the PVC, plasticizers are not chemically bound to PVC polymer, but embedded between the chains of polymer and attached to the PVC net by intermolecular forces.

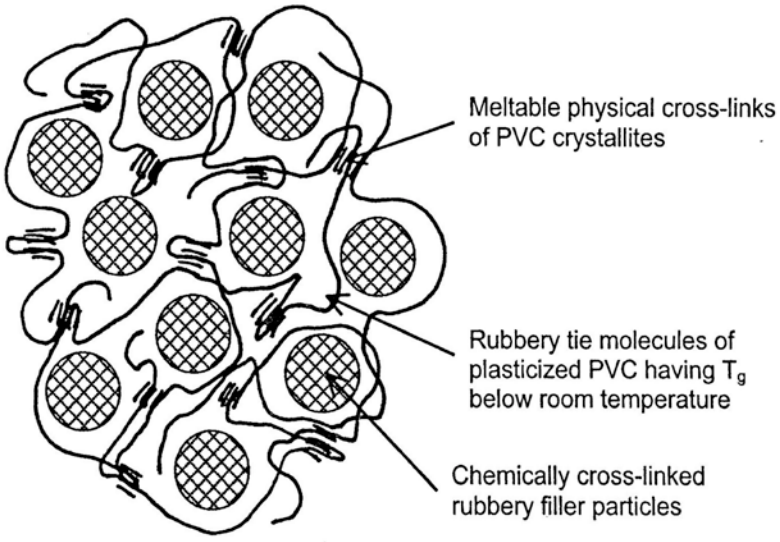


Figure 7: TPE morphology of Plasticized PVC.

The position of the chlorine atom on the hydrocarbon chain leads to highly polar secondary valence forces that allow a high percentage of plasticizers to be bond into the polymer. Even though there is a high diversity of plasticizers that can be added to PVC polymer, the majority belong to the family of *phthalate esters.* Among these, phthalates prepared from alcohols with about eight carbon atoms constitute about 75% of plasticizers used (Brydson, 1999). Commercially, the most common plasticizers used for PVC are: diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and di-2-ethylhexyl phthalate (DEHP, sometimes also referred to as DOP). Furthermore, di-iso-octyl phthalate (DIOP), di- 2-ethylhexyl phthalate (DEHP or DOP) and the phthalate ester of the C7-C9 oxo-alcohol, also unofficially known as dialphanyl phthalate (DAP), have been usually used for economic reasons (Brydson, 1999). Plasticizers different from phthalates are for instance: trimellitates like tri(2-ethylhexyl) trimetillate (TOTM) or tri(isononyl) trimellitate (TINTM); polyesters, formed by esterification of propylebe or butylene glycol with aliphatic dibasic acids; adipates, such as di(2-ethylhexyl) adipate (DOA) or di(isononyl) adipate (DINA); phosphates like tri(2-ethylhexyl) phosphate (TOF) or tricresyl phosphate (TCP) and epoxides, like 2-ethylhexyl epoxy tallate (OET) or epoxidized soybean oil (ESO). Furthermore, other types of plasticizer are those called "phthalate like", which correspond to compounds like esters, benzoates, citrates etc. (Table 5, Wilkes *et al.*, 2005).

Table 5: Plasticizer family/Performance Grid.

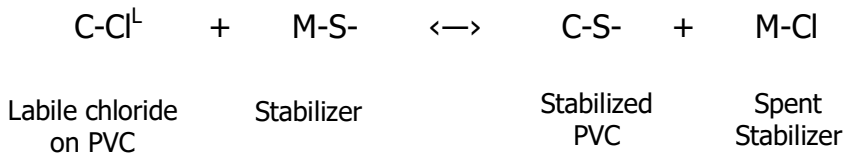
Family	**General purpose**	**Performance plasticizer**			**Specialty plasticizers**		
		Strong solvent	**Low temp.**	**Low volatility**	**Low diffusion**	**Stability**	**Flame resistance**
Phthalates	X	√	√	√	√		√
Trimellitates			√	X	√		
Aliphatic dibasic esters			X				
Polyesters				X	X		
Epoxides			√	√		X	
Phosphates		√	√				X
Extenders	X						

X = Primary performance function √ = Secondary performance function

In addition to plasticizers, **extenders**, can be used in combination with plasticizers despite of their very low compatibility (Chanda and Roy 1998). Typical extenders are chlorinated paraffin waxes, chlorinated liquid paraffinic fractions and oil extracts (Brydson, 1999).

Additives intended to improve the flow of the molten PVC (Chanda and Roy, 1998) are called **lubricants.** These are mainly categorized as internal or external lubricants based on its compatibility with PVC. Lubricants with a moderate compatibility in PVC are characterized as "internal lubricants", such as fatty alcohols, fatty acids, fatty esters and fatty amides, while non- polar waxes, such as paraffin and polyethylene waxes, are incompatible with the PVC and characterized as "external lubricants" (Wilkes *et al.*, 2005). The main function of external lubricants is to prevent sticking of the compound to processing equipment (Chanda and Roy, 1998).

On the other hand, when PVC is heated to 170-180 °C, chlorine and hydrogen in the molecules are eliminated, releasing hydrogen chloride, which causes degradation of the PVC. Since high temperatures are reached during PVC manufacturing (moulding and extrusion), **stabilisers** are added to prevent from HCl loss during the manufacturing process. Thermal degradation of PVC molecules starts at defect structures and occurs until an active stabilizer molecule is close to the site from which labile chlorine releases from PVC by the following mechanism (Wilkes *et al.*, 2005):



The most important class of stabilizers is lead compounds, which form lead chloride upon reaction with the hydrogen chloride evolved during decomposition. Basic lead carbonate (white lead), which has a low weight cost, is the most

commonly used (Chanda and Roy, 1998), although it may release CO_2 and increase the porosity in the product. For this, it has been substituted by other lead compounds like tribasic lead sulfate or dibasic lead phthalate (Chanda and Roy, 2006). However, due to their toxicity, lead-based stabilizers are currently being replaced by compounds of cadmium, barium, epoxides or organo-tin compounds (Brydson, 1999).

Another type of additives added to the PVC in order to prevent from degradation due to heat and light are **antioxidants** and **ultra-violet (UV) absorbers**. Primary antioxidants, typically phenol derivatives, are essentially scavengers of the free radicals, interrupting the progress if oxidative degradation, generally thought to proceed though a free-radical mechanism, although they can improve the heat stability of PVC composition as well as stability to light (Titow, 1984). UV-violet absorbers avoid PVC degradation in the range of 290-400 nm and can be of both inorganic and organic nature. Common inorganic UV-absorbers are for instance titanium dioxide or zinc oxide, which mainly reflects and scatter the incoming UV, IR or visible radiation. Organic UV-absorbers added to PVC are modified benzophenones, benzotriazole derivatives and substituted cyanoacrylates, which absorb incident UV radiation avoiding its damaging action on the PVC material (Titow, 1984).

Fillers are defined in the PVC industry as inert particle solids incorporated into formulations with the purpose of including hardening, stiffening or reduction of volume-cost (Wilkes *et al.*, 2005). Various calcium carbonates (such as whiting, ground limestone, precipitated calcium carbonate) are used for general-purpose work (Chanda and Roy, 1998) and in flexible PVC formulations, plasticizers can enhance PVC capability for uptaking high filler contents (Menges, 1996).

Impact modifiers are generally used as additive in unplasticized PVC in order to overcome problems in processing and high brittleness of finished products. They are generally semi-compatible with the polymer structure and often somewhat

rubbery in nature (Chanda and Roy, 1998). Typical Impact modifiers are (Leadbitter *et al.*, 1994): acrylonitrile-butadiene-styrene terpolymer (ABS), methacrylate-butadiene-styrene termopolymer (MBS), chlorinated polyethylene (CPE), ethylene-vinyl acetate copolymer (EVA) and acrylate polymethacrylate copolymer (ACE).

1.2.4. Degradation

PVC is today mainly used for long-life applications thanks to its excellent cost/performance ratio and outstanding chemical and environmental resistance (Menges, 1996). The presence of chlorine in the polymer provides PVC with fire retardant capacity although this property is reduced by the presence of plasticizers (Brydson, 1999), which also reduce PVC insulation properties, impact strength and water proof attributes (Chanda and Roy, 1998). Carbon-clorine bonds in the PVC can dissociate more easily than carbon-hydrogen ones, due to their lower bond energy and the electric charge dislocation that facilitates the chemical reaction (Wypych, 2008).

PVC polymer is resistant to acids, bases and most of hydrocarbons, although polar solvents may extract plasticiser if present. An extended overview of the chemical characteristics and resistance of both plasticized and unplasticized PVC is shown in Table 6 (Titow, 1984).

Table 6: General chemical characteristics of PVC at room temperature.

Reagents	**Rigid PVC**		**Plasticised PVC**	
	General resistance ratinga[a]	**Remarks**	**General resistance rating[a]**	**Remarks**
Inorganic acids:				
Dilute	S	No attack up to 60°C, but max. allowable design stress should be lowered	S	No significant attack up to 20°C; plasticisers and some fillers may be affected at higher temperatures

Concentrated	S		M	Plasticiser and some fillers may be affected
Oxidising (concentrated)	M	Attacked above 20°C; max. allowed design stress should be reduced substantially	U	Short-term contact may be acceptable in some cases
Organic acids	M		M	
Alkalis:				
Dilute	S	No attack up to 60°C; allowable design stress should be substantially reduced	S	Some plasticisers and fillers may be affected
Concentrated	M		M	
Oxidising agents	S	Allowable design stresses should be substantially reduced	S	Some fillers may be affected
Reducing agents	S	No attack up to 60°C	S	No attack up to 60°C
Detergent solutions	S		S	
Inorganic salt solution	S		S	
Halogens:				
Chlorine	M	Little attack in the absence of moisture	U	
Bromine	U		U	
Fluorine	U		U	
Iodine	U		U	
Aliphatic alcohols	S	Allowable design stresses should be substantially reduced	M	
Water	S	Some softening possible at elevated temperatures	S	Softening, and some effects on certain fillers at elevated tamperatures
Aliphatic hydrocarbons	S		M	Extraction of plasticisers and some effects on other components possible
Aromatic hydrocarbons	U		U	
Chlorinated hydrocarbons	U		U	
Esters	U		U	
Ethers	U		U	
Ketones	U		U	
Aldehydes	M		M	
Amines	M		M	

Liquid fuels	S-M	M-U
Turpentine	U	U
Oils:		
Mineral	S	M-U
Vegetable and animal	S	M-U
Fats	S	M-U

[a]Rating key: S = Satisfactory; M = Moderate (dependent on formulation and conditions); U = Unsatisfactory.

In general, PVC resistance to degradation highly depends on the degradation agent, showing a high vulnerability to any form of oxidation, while it is not affected by hydrolysis or ozone (Table 7, Grattan, 1993).

Table 7. PVC Resistance to Degradation.

Thermal Deterioration of PVC (Maximum Use Temperature for 2. 0 mm film thickness)	**Susceptibility of unstabilized PVC Polymers to Degradation**				
50ºC	**Thermal Oxidation**	**Photo-oxidation Weathering**	**Ozone**	**Hydrolysis**	**Oxidation**
	Very Poor	Poor	Excellent	Excellent	Poor

During processing, storage and utilization, PVC degrades as it is exposed to high temperatures, high mechanical stresses or ultraviolet light, all in the presence of oxygen. However, the light and heat instability of poly(vinyl chloride) is caused by structural abnormalities (defects) that are present to varying extents in different types of commercially available polymer samples. Thus, two major chain processes may occur simultaneously during (photo) (thermal) degradation of poly(vinyl chloride) (Rabek, 1995):

1- Zip dehydrochlorination

2- Oxidative chain processes

In the first process, the degradation of the polymer occurs by successive elimination of hydrogen chloride (HCl), so called dehydrochlorination (mechanism

described in Figure 8 (Rabek, 1996). Once dehydrochlorination is initiated, the progressive unzipping of neighbouring chloride and hydrogen atoms can occur along the polymer chain, forming allyl chloride structures, which is catalysed by release of HCl (Leadbitter *et al.*, 1994). The release of HCl causes the formation of polyene structures $(-CH=CH-)_n$, with n ranging from 2 to 13 (Rabek, 1996), which tend to absorb visible light resulting on the yellowing of the polymer and eventually darken in colour (Lister and Renshaw, 2004). Since main plasticizers in PVC compounds are esters, the production of HCl as a consequence of the dehydrochlorination process may affect their stability by undergoing acid hydrolysis, which will depend on plasticizer type (Wypych, 2013).

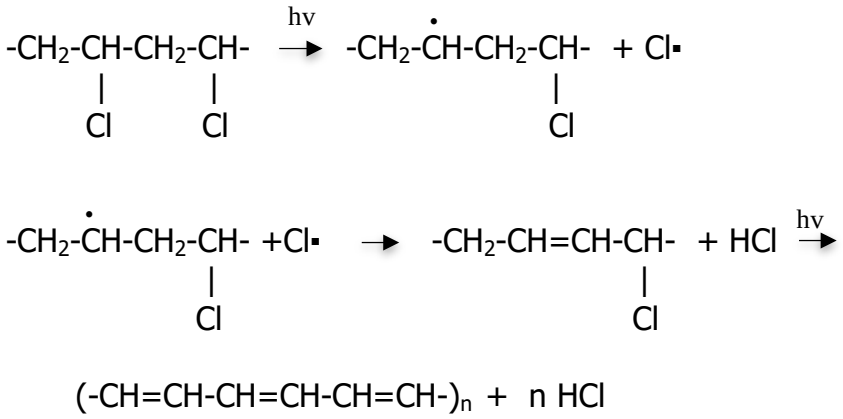


Figure 8. Dehydrochlorination and double bond formation.

Poly(vinyl chloride) contains only C-C, C-H and C-Cl bonds. Therefore, it is not expected to absorb radiation of wavelengths longer than 190 nm, the colour changes of degraded poly(vinyl chloride) is due to the formation of the polyene structures. However, despite of the change of colour, the polyenes form a superficial protective layer that prevents from further degradation of the internal zones, due to their strong absorbance of UV light (Rabek, 1995).

Dehydrochlorination is followed by chain scission and crosslinking of macromolecules (von Hans Zweifel *et al.*, 2009), which finally leads to the embrittlement of the aged material (Owen, 1984), deterioration of the mechanical

properties and a lowering of the chemical resistance (Pauwels, 2004). The second above-mentioned process (oxidative chain processes), leads instead to the formation of hydroperoxide, dialkyl peroxide and carbonyl groups, together with crosslinking and chain scission reactions (Rabek, 1995; Rabek, 1996).

Apart from the PVC polymer itself, another important form of degradation of plasticized PVC is due to the plasticizer loss and migration. The most common way of plasticizer loss is the evaporation from PVC into the surrounding air (volatile loss). Since there is no chemical bonding between the polymer and the plasticizer, evaporation occurs continuously even at low temperatures and it is controlled by the diffusion of plasticizer to the surface and evaporation from the surface (Wilson, 1995).

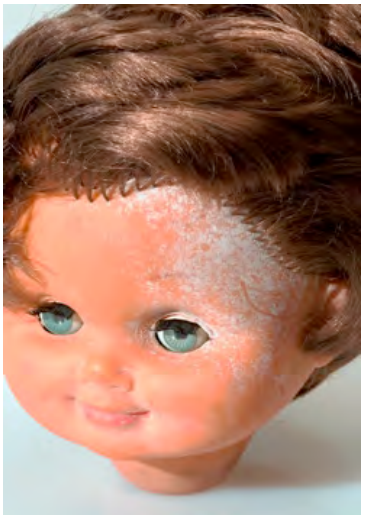


Figure 9. Plasticized PVC doll suffering from migration of additives to the surface.

Both plasticizer loss and migration have been reported to occur in the museum environment. The consequences for PVC objects suffering from these forms of degradation are the formation of sticky surfaces due to the plasticizer migration, as well as becoming more brittle and stiff because of the plasticizer loss (Quye and Williamson, 1999; Shashoua, 2001; Shashoua, 2008; Morgan, 1994). Apart from plasticizer, other additives present in the PVC polymer and added during the manufacturing process may migrate to the surface. They often can be observed as particles settled on the object's surface (Figure 9). In addition, PVC additives may

deteriorate themselves or react with substances in the surrounding, causing the deterioration of the polymer PVC in which they are immersed. Lead stabilizers, for instance, can blacken if exposed to hydrogen sulphide (Morgan, 1994).

Due to the high volatility and their chemical characteristics, plasticizers not only easily migrate from inside the PVC polymer to the surface and evaporate, but also they are easily extracted by organic liquids and solids in contact with it. Water not only reduces the compatibility of plasticizers with the PVC polymer, but does also, when containing surfactants, provides a mechanism for dispersion of the plasticizer as it arrives at the surface and further progressive extraction can then occur (Wilson, 1995). Additionally, plasticizers can easily migrate into solids or polymers next to them, which becomes an issue when plasticizers are in contact with other plastics, like packaging materials or medical devices (Bernard *et al.*, 2015). When aged PVC is handled close to food, plasticizer migration may cause serious Work Health and Safety issues. In museums, damage produced on polystyrene camera bodies by contact with PVC wrist straps has been observed, since plasticiser attacks polystyrene, for which it is a solvent (Morgan, 1994).

Apart from migration from PVC, plasticizers are prone to photo-degradation. In the case of primarily PVC plasticizers, Phthalate Esters, photo-degradation yields to alkenes, alkyl alcohols, phthalic acid anhydride, 2-formyl benzoic acid esters and benzoic acid esters as mayor degradation products, by simultaneous scission of the two esters groups and the cleavage of the C-C bond connecting a carbonyl group with the aromatic ring (Balabanovich and Schnabel, 1998).

On the other hand, by thermal degradation phthalic esters decompose from diester phthalate to monoester phtalate and alcohols. Then, phthalic acid yields to phthalic anhydride at 230º, while alcohols undergo conversion into water and an unsaturated hydrocarbon rest (Figure 10; Wypych, 2013) at determined boiling temperature depending on molecular weight and branching.

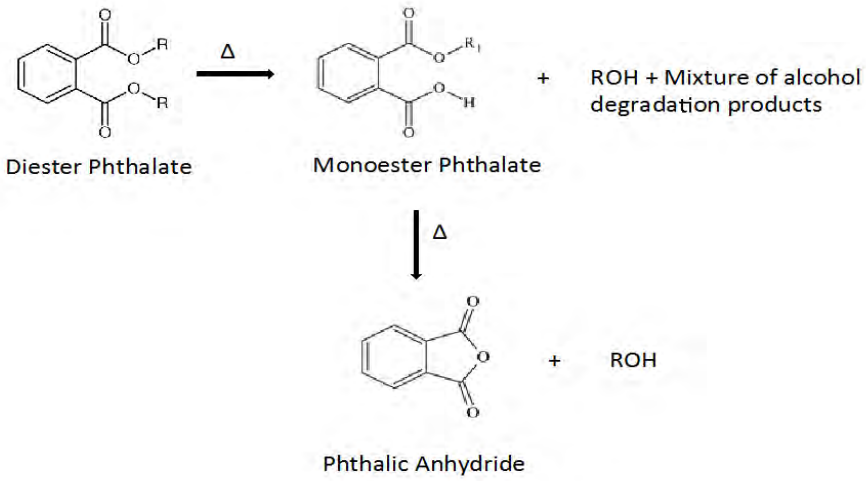


Figure 10. Thermal degradation of phthalic esters.

1.3. Conservation of plastics objects

Within museum collections, plastics can be found as artistic objects themselves (Figure 11), but they are also commonly used in displays or packaging, as well as in restoration treatments as adhesives, for reinforcement etc. (Horie, 1994; Garcia *et al.*, 2009). When including the plastics forming part of artistic objects, a high diversity of plastics compounds can be found in museum collections. (Blank, 1990; Williams *et al.*, 1998; Shashoua, 2001; Quye and Williamson, 1999) This includes but is not restricted to acrylics, polycarbonates, cellulose acetate, cellulose nitrate, nylon (polyamide), polyethylene, polypropylene, phenol formaldehyde, urea formaldehyde, melamine, polyester, polyolefin, polystyrene, polyurethane, poly (vinyl chloride), rubber, etc.

Figure 11. Anders Krisár: "Cuirass" (2005). Oil on silicon and fiberglass.
Photograph courtesy of artist.

Many examples of well-known artists that made extensive use of plastics materials in their work are found within art collections. For example, plasticized PVC was used in artworks performed by Belgian artist Panamarenko (1940), while Naum Gabo (1890-1977) made use of Perspex (trade name for Polymethyl Methacrylate, PMMA) and Nylon (aliphatic polyamide family) in his works. Foams have also been used, e.g. by Dubuffet (1901-1985), who applied expanded polystyrene (EPS) in his sculptures, or Pistoletto, who used polyurethane hard foam is his artwork "Scultura Nera" in 1983 (van Oosten *et al.*, 2002).

From a conservation perspective, plastics are complex compounds which have only been studied relatively recently compared to traditional materials. Interest in their preservation has significantly increased within the scientific community over the last few years (Keneghan, 2005). Dedicated conferences (Grattan, 1993) and international meetings have been held on this particular topic (Keneghan and Egan, 2008), with the purpose of rising awareness within the conservation community on the presence of plastics materials in collections and the growing difficulties surrounding their preservation.

Unlike traditional artwork, many plastics materials easily degrade, what depends on the chemical composition and physical characteristics of the particular polymer. Therefore, specific actions in order to mitigate the risks of degradation must be defined for plastics. Furthermore, the wide range of chemical formulations within plastics leads to many difficulties regarding general conservation and cleaning methods, (Blank, 1990) therefore research into plastics has recently received significant attention (Madden and Learner, 2014)

Studies focused on the investigation and conservation of these particular materials have been developed by specialized researchers with the aim of understanding both the composition and the degradation processes of plastics objects (Shashoua, 2001; van Oosten *et al.*, 2002; Chércoles Asensio *et al.*, 2009), increasing their lifetime within museums and art collections.

Following the definition provided by Salvador Muñoz Viñas, conservation is: "*Any action taken to the end of determining the nature or properties of materials in any kinds of cultural heritage or in their housing, handling, or treatment, any action taken to the end of understanding and controlling agencies of deterioration and any action taken to the end of bettering the condition of such holdings*" (Muñoz Viñas, 2005). It is evident that plastics materials have to be considered part of our cultural heritage and may undergo conservation treatments.

For the conservation of plastics in museums and art collections, one of the most important steps is the identification of the plastic material (Blank, 1990; Williams *et al.*, 1998): the more accurate the determination of the chemical composition, the more precise the conservation approach will be. Due to the complexity of both plastics materials and the techniques used to identify their chemical composition, the determination of the plastics used to create the objects exhibited in museums and galleries is not always possible in situ. For this reason, efforts have been made by researchers in order to provide conservators with simple tools to determine the nature of the plastics objects.

The first step in the identification of polymers is a critical visual examination. While the appearance of the sample may indicate whether it is essentially a raw polymer or a compounded and processed item, learning about its form, feel, odor, color, transparency or opacity, softness, stiffness, brittleness, bounce, and surface texture may be important in the process of the identification of the polymer: polystyrene, for instance, is a transparent and brittle general-purpose polymer that produces a characteristic metallic tinkle when objects molded from it are dropped or struck (Shashoua, 2001). In addition, the visual recognition of moulding marks produced during the manufacturing process may be helpful in the identification of many plastics objects in museums, since certain processes leave marks behind on the finished product and certain plastics are only used with certain processes.

Furthermore, apart from the visual identification, other simple and useful tools often used by conservators to identify the plastic materials are the detection of trade names on the object, (i.e. Bakelite, which is the trade name originally given to the resin produced from phenol and formaldehyde), the study of the physical properties (appearance, flexibility etc.) (Coxon, 1993) or the performance of chemical tests such as: burn test, pH test, solubility tests, density tests and spot tests Coxon, 1993; Williams, 2000) (Table 8).

Other more complex chemical techniques have also been used for the analysis and identification of plastics and its additives in conservation (Quye and Williamson, 1999). Spectroscopic techniques, such as Infrared (IR) Spectroscopy or Raman Spectroscopy and spectrometric ones such as Gas Chromatography-Mass Spectrometry (GC-MS), have been successfully applied to the identification of polymers and plastics additives, and consequently been extensively used for the analysis of plastics objects in the conservation environment (Quye and Williamson, 1999; Seidel, 2008; Koenig, 2008; Shashoua, 2008; Keneghan, 2005; Keneghan and Egan, 2008; Derrick *et al.*, 1999). Other, more recent techniques as for example Tera-hertz (THz) spectroscopy have also been used for conservation purposes on

polymers (Pastorelli *et al.*, 2012). These analytical techniques will be discussed in detail in section 1.4.

Table 8. Spot tests to detect some plastics used in artworks.

Plastic	Spot test	Test result	Reference
Cellulose nitrate	Diphenylamine/sulphuric acid reagent	Colourless to blue solution	Scott Williams *et al.*, 1998.
Cellulose acetate	Alkaline hydroxylamine plus ferric chloride acidified	Burgundy red color develops	Coxon, 1993
Poly (vinyl chloride)	Beilstein test—copper wire heated in torch flame	Colourless flame turns green	Scott Williams *et al.*, 1998.
Sulphur vulcanized rubber (ebonite, vulcanite)	Iodine/sodium azide reagent for reducible sulphur compounds	Bubbles develop in reagent	Daniels and Ward, 1982
Polyurethane	Dimethyl amino benzaldehyde in glacial acetic acid	Canary yellow colour develops	Roff *et al.,* 1971

As above commented, apart from the correct identification of the plastics objects in museums, another significant issue is their degradation. Plastics suffering from degradation problems have been the object of several surveys conducted in museums and collections in recent years (Shashoua, 2001, Morgan, 1991). As mentioned before, degradation processes can be extremely complex and diverse, since they depend on the type of polymer itself. Each type of plastic material has a particular chemical nature that makes it susceptible to specific degradation agents. Thus, under the same environmental conditions, each type of plastic reacts in a particular way. Furthermore, some plastics may undergo chemical degradation while others may experience physical or biological degradation. Degradation processes may change not only the chemical composition, but also the physical characteristics and appearance of the objects (Williams *et al.*, 1998). Plasticized PVC for instance, may undergo degradation under certain light and temperature conditions. These

degradation processes have been identified within collections objects made of plasticized PVC (Shashoua, 2001), causing a risk for their conservation and preservation. In order to prevent further degradation phases, the identification of early stages of degradation by means of regular examination and control of the conservation state of plastics objects becomes essential in museums and art collections.

Degradation in plastics may occur due to several factors like humidity, temperature, pollutants, oxygen, UV radiation or physical forces affecting the plastics materials. The consequences are very diverse and can include: (Shashoua, 2008; Williams *et al.*, 1998; Morgan, 1991; Cheng, 2002; Williams, 1997):

- Changes in colour due to the formation of chromophore groups (e.g. by conjugated double bonds);
- Loss of strength and embrittlement caused by loss of plasticizer and additives or solubility modifications due to crosslinking between the polymer chains;
- Sticky surfaces due to the migration of additives and plasticizer to the surfaces, bloom on the object;
- Attraction of abrasive and hygroscopic particles, such as dust, because of static charges etc.

In the case of PVC, the optical and surface properties are severely modified due to both dehydrochlorination and oxidation processes, which are initiated in the top layer of the material (Owen, 1984). These alterations can be noticed by the yellowing of the surface due to the formation of conjugated double bonds. Also, bleaching of the PVC over time occurs as a consequence of oxidation processes (Wilkes *et al.*, 2005). Plasticized PVC may undergo additives' loss, and in these cases, plasticizers and lubricants can be visually detected on plasticized PVC surfaces, indicating degradation (Shashoua, 2008).

In order to preserve plastics in museums, researchers have looked for general guidelines that help conservators and restorers to preserve these particular

materials. Some of the recommendations found in the literature (Quye and Williamson, 1999; Blank, 1990; Williams *et al.*, 1998; Morgan, 1991) are:

  - Minimum exposure to light (50-100 lux) in order to avoid photo-degradation;
  - Stable and controlled relative humidity (equal to or below 55% depending on the susceptibility of the plastics) in order to prevent hydrolysis;
  - Stable and controlled temperature (within 15-20 Celsius) in order to avoid thermo degradation effects;
- Ventilated spaces in exhibition and storage areas in order to avoid vapours from some plastics affecting other plastics nearby;
- Controlled cleaning to prevent degradation caused by contaminants;
- Avoidance of contact between plastics to prevent the migration of additives from one plastic to another;

Last but not least, it must be pointed out that in the field of conservation not only the preservation of plastics objects, but also the health of conservators dealing with plastics materials in the museum environment has become important. Since vapours released by degraded plastics, additives which have migrated to the surface of other objects or plastic degradation products may become toxic for people working with plastics, several authors have aimed to prevent negative health consequences for restorers, conservators and those directly exposed to or in contact with degraded plastics by providing practical guidelines for the safe handling of plastics (Tsang, 2010).

Summarizing all of the above-mentioned aspects concerning plastic conservation, it could be stated that by "*employing the growing physical and chemical knowledge about plastics, a conservation plan and a collection management strategy can be developed for modern art containing plastics*" (van Oosten *et al.*, 2002). Within the framework of actions this requires, the methods for cleaning of plastics objects can be considered to be the less general applicable and have to be tailor made for each group of polymer formulation.

1.3.1 Cleaning of Plastics Objects

The first definitions of cleaning and patina related to works of art were given by Tuscan artist Filippo Baldinucci in the late 17th century. In his Italian dictionary, to clean ("pulire") does not only mean to take away dirt and stains, but also "*to polish, mainly marble and metal*". The "patena" which may be removed by this action is defined as a visual change time caused on the object, but which may also favour the artwork, clearly pointing to the central conflict of any restoration action (Baldinucci, 1681). For decades, cleaning art objects has been subject to discussion in conservation and restoration manuals, while many theories and essays have approached the main concepts regarding "art works cleaning" in terms of conservation theory (Brandi, 1977; Baldini, 1997). From a logical point of view, the first question to consider should be "Why clean an art object"?

The first and most intuitive answer to this question is to assume that the cleaning action improves the object's appearance and significance, recovering the initial purpose of the artist by exhibiting an object close to the original. This is however also the most controversial answer, which has led to long discussions about aesthetic intervention by the restorer and the subsequent consequences for the art object (Hedley, 1986). Over decades, the cleaning of famous masterpieces has been debated, leading to a strong divide between those who support the applied treatments and those who criticise these methods (Keck, 1984). Throughout conservation history, many authors have raised their voices to criticise over-cleaning or inadequate cleaning policies. Umberto Baldini in his "*Teoria del restauro e unità di metodología*" (Baldini, 1978) for instance recommends balanced cleaning treatments that respect the original surface and the passage of time on the material. He also points out the importance of preserving the historicity of the object. Thus, excessive cleaning should be avoided or at least reflected upon in order to avoid "wiping out" the inherent characteristics of an artwork. Furthermore, in a more theoretical manner, Cesari Brandi states in his well-known "*Teoria del Restauro*" that any restoration treatment should focus on the potential recovery of the artwork, but

respecting signs of the passing of time on the artwork (Brandi, 1977). This statement includes all restoration treatments, of which cleaning is a fundamental part.

Over the past decades, the most famous examples of controversial cleanings include the Michelangelo´s Sistine Chapel and Leonardo Da Vinci´s Last Supper, as well as an excessive and unauthorised cleaning of the Parthenon Marbles in 1937-1938 at the British Museum of London, which was only recently extensively documented (Jenkins, 2001).

Even though plastics are relatively recent materials, recommendations for their cleaning in museums can be found in literature, in agreement with the general conservation theories illustrated above. In 1994, for example, John Morgan referred to cleaning methods for plastics when he stated that: "*cleaning procedures carry with them an associated risk of damage and the methods employed must be carefully considered and controlled*" (Morgan, 1991). Since then, other authors and institutions have been actively investigating conservation treatments for plastics (Quye and Williamson, 1999; Shashoua, 2001; Williams, 2000; Grattan, 1993; van Oosten *et al.*, 2002; Keneghan, 2005; Keneghan and Egan, 2008). This on-going investigation will be further developed in the following section of this chapter.

The second answer to the question proposed above is related to the positive effect that cleaning treatments have regarding the conservation of works of art. First of all, it is generally accepted that the removal of dirt from the objects' surfaces reduces the risk of potential deterioration. This is mainly due to the fact that mechanical damage caused by erosive substances settling on the surfaces of the plastics objects is avoided by the removal of these harmful particles. Furthermore, cleaning treatments may slow the rate of chemical deterioration by removing dirt, since particles of dust, skin flakes or grease, among other substances, could act as a medium for water and acid pollutants to stay on the objects' surfaces. In the particular case of plastics materials, cleaning has been identified as a potential "conservation element" not only for the removal of pollutants and erosive particles,

but also because decomposition products accelerate deterioration and, in many cases, degradation is initiated by contaminants, such as oxygen and metal ions, on the surface of the object (Morgan, 1991).

Taking the previous arguments into account, it does seem clear that cleaning processes are a significant step forward in the future preservation of cultural heritage. Nevertheless, an important aspect of the cleaning process must also be taken into consideration when cleaning an artistic object: "secondary effects". Like any other cleaning treatment in conservation, the cleaning of a plastic object must guarantee that no immediate or long-term damage is produced as a consequence of the cleaning treatment. This means that the removal of dirt should be approached in a way that ensures minimum risk for the plastic object itself. Unlike cleaning methods for other traditional materials used in art, such as paint and stone, safe cleaning methods for plastics compounds must deal with a wide chemical diversity. This increases the difficulty of finding safe cleaning methods that can be applied to all types of plastic materials. Additionally, it has to be considered that plastic materials are highly susceptible to degradation and therefore they are often found in degraded conditions within art collections and museums (Shashoua, 2001). This fact requires conservators to search for more specific cleaning treatments that safeguard plastics objects regardless of their chemical composition or conservation status (from non-degraded to degraded).

1.3.2 Cleaning Methods

In order to achieve successful results with a cleaning method, the first step in the methodology is the identification and characterization of both the material that is going to be cleaned and the substances that are going to be removed. Regarding the particles to remove, these could be originated from all of the different environments that the object has been exposed to during its lifetime and can therefore include a wide range of compounds. Pre-collection use of the object may, for example, may be

the cause of finger marks and grease on the object. Also, dust, dead skin cells, sand, pollutants or microbiological specimens (Nazaroff, 1993; Hun Yoon and Brimblecombe, 2001a) may be deposited on the object during its exhibition, whether due to visitors or the museum environment itself. Furthermore, traces of packaging materials from storage or remnants of restoration treatments can be found on the objects' surfaces, while it may be necessary to remove a wide variety of degradation products from the plastics objects, depending on their degradation stage.

The second step when selecting a specific cleaning method for a plastic object is considering the type of cleaning that is going to be performed. There are several classifications within cleaning methods: all of them refer to differences between practical aspects of the cleaning. For example, one widely used classification is the distinction between *"mechanical"* and *"chemical"* cleaning methods (Wilks, 1987). Mechanical cleaning methods refer to "breaking the adhesion of the dirt and moving it away" from the object and includes a large list of abrasive agents (such as sand particles), (physical cleaning by non-contact with the surface of the art object), air canisters, vibrations (e.g. ultrasound vibrations), cloths, vacuum cleaners etc. Chemical cleaning methods involve chemical reactions that break the bonds within particles (dirt-dirt bonds or dirt-object surface bonds), such as the reactions produced by water, detergents, solvents, commercial cleaners, gels, etc. Another general approach is the classification of *"wet"* and *"dry"* cleaning methods (Saulnier, 2002). Following this approach, dry cleaning methods are those that do not involve liquids but instead include the use of abrasive particles, sponges or cloths. On the other hand, wet cleaning methods are based on the use of liquids, such as water, detergent solutions, organic solvents, commercial cleaners etc. Within wet cleaning methods there is a sub-category, which refers to the use of water or organic solvents. This sub-classification can be defined as *"organic solvent-based"* and *"water-based"* cleaning agents.

Outside the previous classifications there are other particular types of cleanings: the use of biological agents named *"enzymes"* and the cleaning based on the use of

lasers. The enzymes are natural proteins that catalyse reactions in live organisms. Due to the selectivity of enzymes in this catalytic action, some of them have been used to "break down" other organic materials in order to remove them from the artistic object. Enzymes act only upon a particular type of molecules (named "substrate") without affecting other organic materials of different nature. Enzymes used in restoration are *proteolytic*, *lipolytic* and *glycosidic enzymes* that catalyse the hydrolysis of chemical bonds of proteins, lipids and polysaccharides, respectively. Due to this property, these enzymes may be used as an alternative to acids and bases for the cleaning of old polymeric substances on the artworks, such as natural adhesives, casein films, varnishes etc. (Cremonesi, 1995). On the other hand, lasers are based on the utilization of pulsed laser radiation for ablation, allowing the precise control of surface cleaning level. Lasers are devices which coherently emit light, allowing to focus it on a very small spot. Light emission is based on the process of stimulated emission of electromagnetic radiation and characterized by high intensity, monochromaticity (emission in a very narrow wavelength) and directionality (Fotakis *et al.*, 2006). The fundamental parameters for a laser ablation cleaning method are: the absorption coefficient in the material to be removed, which depends on the wavelength of emitted laser radiation and the magnitude of the laser energy focused on the specimen (expressed in J/cm^2). These two quantities determine the efficiency and surface cleaning level (Koss and Marczak, 2005). Though useful in other areas of cultural heritage, this technique is not very suitable for plastics substrate since the damage thresholds are fairly low. When cleaning plastics, due to their particular chemical and physical properties, several factors should be initially considered before selecting a cleaning method, in order to avoid adverse results. These factors are:

- Chemical Resistance of the polymer;
- Temperature during cleaning;
- Surface tension of the chosen solvent on the substrate;
- pH;
- Solubility of polymer in cleaning solution
- Solvent volatility;
- Cleaning time.

Chemical Resistance refers to the chemical reaction a specific polymer undergoes by the action of certain chemical agents. Although resistance against attack by chemicals, environments and radiation greatly depends on the chemical nature and bonding, it depends even more on weak links in the polymer chain, such as chemical defects in the chain, branch points and polymer end groups (Lampman, 2003). For example, hydrolytic breakdown is a major pathway for semi-synthetic polymers, (cellulose nitrate or cellulose acetate), and consequently aqueous cleaning should be avoided when cleaning artworks made of these polymers (Keneghan and Egan, 2008). When cleaning plastic artworks, the reactivity of the plastic under cleaning treatment must be considered and investigated in order to avoid damages during the cleaning process.

"*Plastics are hard rigid solids at sufficiently low temperature, but when the temperature rises, thermoplastic polymer eventually acquires sufficient thermal energy to enable its chains to move freely enough to behave like viscous liquid, assuming there is no degradation*" (Chanda and Roy, 2006). According to this, any process involving changes of temperature in polymers must be controlled since they can affect the physical structure of the polymer. Effects on polymers due to temperature changes depend on the range of temperatures reached. There is a number of temperature definitions associated to phase transitions of polymers. At the Glass Transition Temperature (T_g), micro mobility of chain segments and side chains starts to occur and thermoplastics become softer but they are still mechanically stable.

Above T_g, the molecular mobility increases, diminishing the mechanical strength of the polymer (Klein, 2011). This means that polymers behave like rubber above T_g while they become rigid and brittle below the T_g. On the other hand, crystalline thermoplastic polymers melt when exceeding the Crystalline Melting Temperature (T_m) while amorphous thermoplastic resins reach the molten phase when above the Flow Temperature (T_f). Having reached a molten state, the degradation of both

amorphous and crystalline thermoplastics starts above the decomposition temperature T_d (Klein, 2011). On the contrary, thermoset polymers do not have a T_m and instead of softening above T_g, they burn (Gómez Gonzáles, 1994).

Table 9. Glass Transition Temperatures (T_g) and Crystalline Melting Temperatures (T_m) of polymers.

Polymer	**T_g (°C)**	**T_m (°C)**
Polyethylene	-125	137
Polyoxymethylene	-83	181
Polyisoprene (natural rubber)	-73	28
Polyisobutylene	-73	44
Polypropene	-1	176
Poly(vinylidene chloride)	-18	200
Poly(vinyl fluoride)	41	200
Poly(hexamethylene adipamide) (nylon-6,6)	50	265
Poly(ethylene terephthalate)	61	270
Poly(vinyl chloride)	81	273
Polystyrene	100	250
Poly(methyl methacrylate)	105	220
Cellulose triacetate	105	306
Polytetrafluoroethylene (Teflon)	117	327

Since some plastics have T_g close to ambient temperature (Table 9) (Odian 2004), any cleaning method involving mechanical actions (friction) and temperature increase should be tested beforehand in order to avoid melting, deforming or scratching the plastics' surfaces due to heat produced during the cleaning (Chanda and Roy, 2006). Since scratches are areas vulnerable to chain scission and of higher reactivity due to the increase of surface area, they would be particularly prone to a reduction in tensile strength and eventual failure of the polymer network, as well as to a reduction in gloss due to the decrease of the light reflective properties of surfaces (Keneghan and Egan, 2008).

Surface Energy is another important property to take into account when considering the cleaning of a plastics object, since it is related to the wetting of a

surface (De Gennes *et al.*, 2004). Wettability is the tendency of a liquid to spread on a solid substrate (Fujinami *et al.*, 2009). Wettability depends on the relation of the surface energies of substrate and the surface tension of the solvent. To wet, the surface tension, of the solvent must be low compared to the surface energy of the substrate (Table 10).

Table 10. Surface free energy of polymers and surface tension of solvents.

Polymer	**Surface free energy at 20 °C [mN/m]**	**Solvent**	**Surface tension at 20 °C [mN/m]**
Polyamide-6,6 PA-66	46.5	Water	72.8
Polyvinylidene chloride PVDC	45	Glycerol (GLY)	64
Polyethyleneterephthalate PET	44.6	Formamide (FA)	58.2
Polyethyleneoxide PEO	42.9	Diethylene glycol (DEG)	44.8
Polyetheretherketone PEEK	42.1	Ethylene glycol (EG)	47.7
Polyvinylchloride PVC	**41.5**	Nitrobenzene	43.9
Polymethylmethacrylate PMMA	41.1	Carbon disulfid	32.3
Polyamide-12 PA-12	40.7	1-nitro propane	29.4
Polystyrene PS	40.7	Ethylbenzene	29.2
Polyvinylacetate PVA	36.5	Benzene	28.88
Polyethylene-linear PE	35.7	Chloroform	27.5
Polyethylene-branched PE	35.3	Tetrahydrofuran (THF)	26.4
Polycarbonate PC	34.2	Acetone (2-Propanone)	25.2
Polyisobutylene PIB	33.6	Methyl ethyl ketone (MEK)	24.6
Polypropylene-isotactic PP	30.1	Propanol 25 °C	23.7
Teflon™ PTFE	20	Methanol	22.7
Polydimethylsiloxane PDMS	19.8	Ethanol	22.1

For example, in the case of PVC, its surface energy is lower than the surface tension of water (Table 10), and no wetting is produced (Figure 12). On the contrary, surface tension of ethanol is half of the surface energy of PVC (Table 10). Therefore, ethanol spreads on the PVC surface (Figure 12).

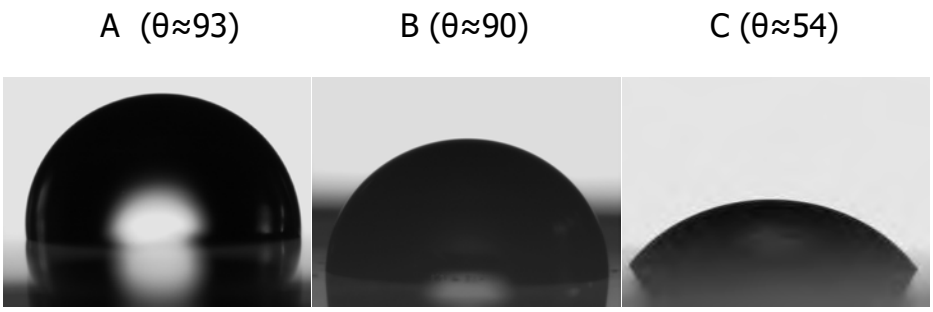


Figure 12. Contact Angle measurements of deionized water (A), KOH 1N (B) and Dehypont LS45 5% (C) on plasticized PVC.

Many plastics have a low surface energy, and therefore have notoriously low critical wetting tensions (Goss, 2010), which makes it difficult to wet their surfaces. The surface energy (measured in mN/m) of a given surface is usually calculated by measuring the contact angle (θ) with a liquid of known tension, and this can be affected by the interfacial tensions and certain characteristics of the polymer, including: surface roughness, chemical heterogeneity, swelling and partial solution of the polymer, molecular orientation, etc. (Augsburg, 1998). Contact angle, defined as the angle formed between the liquid-vapour and the liquid-solid interfaces at the solid-liquid-vapour three-phase contact line, is a measure of the hydrophobicity and wettability of a surface (Pesonen-Leinonen, 2005). When the contact angle value is smaller than 60º, the surface tends to be completely wetted. Poor wettability of a surface occurs when the contact angle is higher than 90º. The wettability of a surface also depends on the polarity of the solvent or liquid used for the cleaning. Plastics are mainly hydrophobic, therefore non-polar organic solvents tend to wet plastic surfaces better, while water or polar solvents tend to form sphere drops on the surface, making contact between the plastic solid and the cleaning solution difficult.

A practical example characterizing the wetting behaviour of liquids on a commercial plasticized PVC surface by means of contact angle (θ) measurements, calculated with the pendant drop method, illustrates the differences between several

solutions. While deionised water produces a poor plasticized PVC wettability (high θ values) and tends to form drops on the plastic's surface, basic or detergent aqueous solutions diminish the θ, increasing the surface of solid and liquid in contact (Figure 12).

Therefore, cleaning agents recommended for use on plastics surfaces must have a surface tension lower than the plastic in need of cleaning in order to achieve the necessary contact between both surfaces required for the cleaning process to happen. However, there are other factors that affect the wettability of a surface by a liquid which need to be considered when cleaning a surface. For instance, not only surface tension, but also the viscosity and density of the liquid are important properties that will affect the spreading capacity of the liquid. Surface roughness and the quantity of impurities also affect the wettability, while temperature can modify the viscosity of the liquid and therefore the ease with which it spreads out over a surface (Kumar and Prabhu, 2007). All of these external and internal factors inherent to the surfaces should be taken into account during any cleaning process.

Furthermore, degradation of polymers can be caused by chemical reactions like hydrolysis (Chanda and Roy, 2006). Polymers containing hydrolysable groups such as esters, amides and carbonates are susceptible to water attack. When these groups are present in the main chain, their hydrolysis will result in a reduction of molecular weight and initiate the deterioration of the polymer (Brydson, 1999). The rate of hydrolysis directly depends on the pH (Leeuwen and van Vermeire, 2007), since acids and bases catalyse hydrolysis reactions. Thus, the pH of the cleaning solutions must be controlled in order to avoid damage to the plastic object during the cleaning process.

Solubility is defined as the maximum amount of solute that can be dissolved in a given amount of solvent (Wilks, 1987). For a substance to be soluble in solvent, the forces of attraction between the solvent molecules and the substance should be higher than the forces of attraction between the molecules within the substance.

When using cleaning solutions, only dirt should be dissolved during the cleaning process whilst the matrix artwork material should remain unaffected. In order to avoid the undesirable dissolution of the artwork´s material components, the "*Hildebrand Solubility Parameter*" is used to predict the solubility of a substance into a particular solvent (Table 11). The "Hildebrand Solubility Parameter", (δ, expressed as $MPa^{1/2}$ in SI units) is defined as the square root of the cohesive energy density and is a direct reflection of the degree of van der Waals forces holding the molecules of the liquid together (Burke, 1984). δ can be expressed as:

$$\delta = [(\Delta H_v - RT)/V_m]^{1/2}$$

where ΔHv is the enthalpy of vaporization and Vm the molar volume. R is the universal gas constant and T the absolute temperature, this term is subtracted from the enthalpy of vaporization to obtain an energy of vaporization (Belmares *et al.*, 2004).

Table 11. Hildebrand Solubility Parameters for some common solvents.

Solvent	**δ, $(MPa)^{1/2}$**
n-Hexane	14.9
Toluene	18.3
Benzene	18.7
Acetone	19.7
Ethanol	26.2
Methanol	29.7
Water	48.0

The Hildebrand Parameter has been calculated for many solvents (Table 11, Burke, 1984) and substances, including plastics materials (Table 12, Rudin and Choi, 2012), and is based on the following principle: "two compounds are soluble only when their solubility parameters are close to each other". In other words, the further apart the plastic and the solvent's Hildebrand parameters are, the smaller the risk of the plastic dissolving. In the case of plastic objects, not only the solubility of the

plastic material itself, but also the solubility of the additives that make up the total material, should be considered.

Thus, cleaning solvents and cleaning solutions should be selected according to: 1) the solubility of the particles that should be removed from the object; 2) the solubility of the plastic in need of cleaning and 3) the solubility of the plastic's additives. This means that solvents or cleaning solutions selected for the cleaning should solve the dirt or particles that are aimed to be removed and should not dissolve either the polymer network or any other compounds in the polymer's composition, such as additives (i.e. plasticisers). According to the values shown in Tables 11 (Burke, 1984) and 12 (Rudin and Choi, 2012), for instance, Poly(vinyl chloride) has a similar solubility parameter to acetone. This means that acetone would never be recommended for the cleaning of this polymer because it would dissolve it, causing irreversible damage.

Table 12. Hildebrand Solubility Parameters for some common polymers.

Polymer	**δ, $(MPa)^{1/2}$**	**H-Bonding Group[a]**
Polytetrafluoroethylene	12.7	Poor
Polyethylene	16.4	Poor
Polypropylene	17	Poor
Polyisobutylene	17	Poor
Polybutadiene	17.2	Poor
Polystyrene	18.4	Poor
Poly(methyl methacrylate)	19.0	Medium
Poly(vinyl acetate)	19.7	Medium
Poly(vinyl chloride)	19.9	Medium
Cellulose diacetate	23.3	Strong
Poly(vinyl alcohol)	26.0	Strong
Polyacrylonitrile	26.0	Poor
Nylon-6,6	28.0	Strong

a Composition of copolymers are in parts by weight

An extension of the Hildebrand Parameter is the Hansen Parameter (Hansen, 1967) (Table 13) (Burke, 1984). It considers not only the dispersion forces (δ_d^2), but also the hydrogen bonding (δ_h^2) and polar components (δ_p^2) (Leeuwen and van Vermeire, 2007; Belmares *et al.*, 2004). Thus, the Hansen Total Cohesion Parameter is the sum of these three components:

$$\delta_t^2 = \delta_d^2 + \delta_h^2 + \delta_p^2$$

Table 13. Hansen Solubility Parameters and Interaction Radius for some polymers and resins.

Polymer (trade name, supplier)	**δd $(MPa)^{1/2}$**	**δp $(MPa)^{1/2}$**	**δh $(MPa)^{1/2}$**	**R $(MPa)^{1/2}$**
Cellulose acetate(Cellidore® A, Bayer)	18.6	12.7	11.0	7.6
Chlorinated polypropylene(Parlon® P-10,Hercules)	20.3	6.3	5.4	10.6
Epoxy (Epikote® 1001,Shell)	20.4	12.0	11.5	12.7
Isoprene elastomer (Ceriflex®IR305, Shell)	16.6	1.4	-0.8	9.6
Cellulose nitrate1/2 sec,H-23, Hagedorn)	15.4	14.7	8.8	11.5
Polyamide, thermoplastic (Versamid® 930, General Mills)	17.4	-1.9	14.9	9.6
Poly(isobutylene)Lutonal® IC-123, BASF)	14.5	2.5	4.7	12.7
Poly(ethylmethacrylate)(Lucite® 2042, DuPont)	17.6	9.7	4.0	10.6
Poly(methyl methacrylate)(Rohm and Haas)	18.6	10.5	7.5	8.6
Polystyrene (Polystyrene LG, BASF)	21.3	5.8	4.3	12.7
Poly(vinyl acetate)(Mowilith® 50, Hoechst)	20.9	11.3	9.6	13.7
Poly(vinyl butyral)(Butvar®B-76, Shawnigan)	18.6	4.4	13.0	10.6
Poly(vinyl chloride)(Vilpa® KR, k=50, Montecatini)	18.2	7.5	8.3	3.5
Saturated polyester(Desmophen® 850, Bayer)	21.5	14.9	12.3	16.8

The Hansen solubility parameters are determined empirically based on multiple experimental solubility observations. However, for polymers the Hansen parameters are assigned to the parameters of the solvent causing the maximum swelling in a series of polymer swelling experiments. Thus, the Hildebrand and the Hansen parameters are expected to be similar but not identical, because the Hildebrand

parameters are not always determined from enthalpies of vaporization, particularly for substances with high boiling points (Belmares *et al.*, 2004). Although the Hildebrand and Hansen Parameters are both used to express solubility, their values may not be identical since they have been calculated by different methods (Chanda and Roy, 2006).

When the three Hansen Parameters are treated as coordinates to define a point in three dimensions, we obtain the center of a solubility sphere (δ_d, $\delta_{p,}$ δ_h) and its corresponding radius of interaction (R). Liquids whose parameters lie within the volume are active solvents for that polymer. A polymer is probably soluble in a solvent (or solvent blend) if the Hansen parameters for the solvent lie within the solubility sphere for the polymer (Burke, 1984). Solvents with similar Hansen solubilities are miscible in most proportions; dissimilar values yield limited solubilities. Hildebrand and Hansen solubility parameters are useful for selecting solvents and additives in formulations, for the blending of polymers, for the control of kinetics and monomer sequence distributions in copolymers (Belmares *et al.*, 2004).

Another key factor in any cleaning process is solvent **volatility**. The volatility of a solvent depends on its viscosity and surface tension. Thus, liquids that have a low viscosity and low surface tension tend to have a high volatility and therefore the duration of contact between the liquid and the surface in need of cleaning is short. On the other hand, liquids with a high viscosity and high surface tension have a low volatility and this allows them to interact for a longer period of time with the surface (Wilks, 1987). In order to assess the rapid evaporation of solvents, the vapour pressure, the boiling point and the latent heat are taken into account. Thus, the higher the Vapour Pressure and the lower the boiling point and latent heat, the more volatile is a solvent (Gómez Gonzáles, 1994). In some cases, prolonged cleaning is necessary in order to remove the dirt from the surface and techniques, such as *solvent- based gels* (Stulik *et al.*, 2004; The Getty Conservation Institute, 2015), developed by Richard Wolbers are used to decrease the volatility of the solvent and offer important benefits such as the cleaning of surfaces that could not be cleaned by

traditional solvent or mechanical methods and a more controlled and selective cleaning than other methods.

When cleaning plastics, the **cleaning time** (the duration of the contact between the liquid and the plastic undergoing the cleaning) must be monitored due to its direct impact on the material, both negative and positive. Despite of being prolonged cleanings possibly more efficient removing dirt than short cleaning times, long ones may produce adverse consequences for the plastics surfaces. For instance, objects may absorb cleaning solutions if these stay prolonged time in contact with the object's surface or the object is immersed in the cleaning solution. This is the case for polyvinyl chloride, which is insoluble and chemically stable in water, yet it absorbs water and swells when immersed for a prolonged period of time (Sale, 1988). Another adverse effect of prolonged cleaning treatments is the extraction of plastics' additives by solvents or detergent solutions. Likewise, the risk of damaging increases with the cleaning time when using dry cleaning methods. Plastics' cleaning by means of cloths or soft brushes, for instance, may detach particles from the object during the cleaning action and hold them in the cloth or brush material, then scratching the plastics surface upon further use. In these cases, it is important not only to select short cleaning times but also to replace the cleaning agent if longer cleaning is needed.

Given all the above considerations, it becomes clear that the main problem when cleaning plastic objects in museums is determining which method (mechanical, water or solvent-based, chemical etc.) can be effectively used without damaging the object. Within conservation, general and specific treatments can be found in reference to the cleaning of plastics objects. After reviewing these treatments, the following general recommendations can be extracted:

- Deionized water has been generally recommended for plastic cleaning (Fairbrass, 1999; Shashoua, 2008) although there are authors who recommend caution, especially when immersing the plastics objects in water (Sale, 1988) and some even advise against using this solvent for cleaning plastics and rubbers;

- Organic solvents, which are usually used in conservation for cleaning, are not recommended for cleaning plastics, due to risks of swelling, dissolving and extracting additives from plastics (Sale, 1988, Shashoua, 2008) although their use for specific cleaning purposes (such as the removal of old labels and traces of adhesive from previous restoration work) has been proposed and accepted by several researchers (Quye and Williamson, 1999; Shashoua, 2008; Huys and van Oosten, 2005);
- Detergent solutions have been suggested as cleaning solutions for plastics, although some authors have warned about negative effects on certain types of plastics. The use of low concentrated detergent dilutions and their complete removal from the plastic surface after the cleaning process has been strongly advised (Sale, 1988; Blank, 1990; Quye and Williamson, 1999);
- Dry cleaning (cotton swabs, brushes, cloths, vacuum cleaning, etc.) has been generally accepted as a safe practice for the cleaning of artworks made of plastic (Williams *et al.*, 1998; Shashoua, 2008). Furthermore, some authors suggest that dry cleaning is the "best method" for cleaning plastics and rubbers (Williams, 1997);
- The immersion in baths and prolonged rinsing of the plastics objects subjected to the cleaning has not been recommended. Cleaning solutions have been suggested to be carefully applied and quickly removed (Quye and Williamson, 1999);
- Commercial polishes have been accepted within the conservation community, although with much controversy. Some authors have recommended their use for plastic cleaning (Budden, 1991) while others have suggested precaution when used on plastics objects in museums (Shashoua, 2008), since the full range of possible consequences has not yet been fully investigated.

In the particular case of PVC artworks, wet cleaning methods have been proposed by several authors, although these are generally accompanied by mechanical action, since solvents or cleaning solutions need a carrying medium such as cotton swabs to be applied. In some cases, wet cleaning may be performed with

no-mechanical actions involved, like cleaning by immersing the artwork in a cleaning solution or solvent, although this has been not recommended for PVC due to undesirable effects such as solvent swelling or additives migration (Sale, 1988).

The most common wet cleaning method advised for PVC objects in conservation is the cleaning by means of deionized or demineralized water (Fairbrass, 1999; Shashoua, 2008). Furthermore, some authors have proposed surfactants for PVC cleaning, such as aqueous solutions of non-ionic detergents (Fairbrass, 1999; Huys and van Oosten, 2005) like Synperionic N (C_9H_{19}-C_6H_4-(CH_2CH_2O)n-OH) or Dehypon LS 45 (fatty alcohol alkoxylate, C_{12}-C_{14} with approximately 4 moles Ethylene Oxide and approximately 5 moles Propylene Oxide).

The use of organic solvents has not been advised for PVC cleaning due to the interaction with the plastic or its additives (Sale, 1988). Acetone, for instance, is able to dissolve PVC and should be avoided for PVC cleaning (Shashoua, 2008). However, some organic solvents have been proposed to remove degraded adhesives and remains of previous restorations from PVC artwork´s surface, such as xylene or ShellSol A100 (Huys and van Oosten, 2005). Based on aqueous methods used in Conservation for cleaning painting surfaces (Wolbers, 2000), recent investigations have studied the use of water microemulsions with a surfactant and an organic solvent with a very different solubility parameter to the PVC to clean flexile PVC (Hackett, 2014), which opens new possibilities in the use of mixtures for the cleaning of PVC artworks. An example of these mixtures is Ecosurf 3, a non-ionic low HLB (Hydrophilic–Lipophilic Balance) surfactant, decamethylcyclopentasil (a non-polar solvent) and deionized water.

1.4. Analytical techniques for polymers

As explained in previous chapters, detailed information of the composition of a work of art is needed for its conservation. Furthermore, any artistic object that is going to undertake a restoration treatment must be carefully examined and analyzed before the application of the treatment. Only in this way, it is possible to prevent it from irreversible damages or the modification of the artwork material. When analysing an artwork, the subtraction of any piece of the artistic object for the analysis should be avoided as far as possible, being only carried out when absolutely necessary. In these cases, sampling is mostly done in hidden parts of the artwork and by taking pieces, which are already detached from the original.

Based on the impact that the sampling has on the original artworks, analytical techniques can be divided into two main categories: *destructive* and *non-destructive* techniques. Non-destructives techniques are those that allow analytical information to be obtained with no damage to the sample or (in some cases) to the artefacts in question (Janssens and Van Grieken, 2004). In other words, when using a non-destructive technique the sample can be used again for the analyses, since neither destruction nor modification of the sample has been produced. Examples of non-destructive analysis are Attenuated Total Reflection (ATR) Spectroscopy, X-ray Diffraction (XRD) or X-ray Fluorescence (XRF). Furthermore, non-destructive techniques may be classified between *non-invasive*, when sampling and further treatment of the object is not required and invasive when it is required. Scanning electron microscopy (SEM), for instance, is an invasive technique because it needs both sampling from the object and sputtering (at least for non-metallic samples such as polymers), even though the sample may be re-analysed if needed. Differently, ATR- Fourier transform infrared (FTIR) spectroscopy is a non-invasive technique, since it can be directly applied on the artworks surface, with no sampling requirement. On the other hand, destructive techniques are those that involve sampling from the object and consumption of the sample during the measurement. These methods are, for instance, chromatographic techniques (gas chromatography,

GC, liquid chromatography, LC, gel permeation chromatography, GPC), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), etc. due to the need of the sample preparation (e.g. digestion) or the destruction of the sample during the analysis. Within destructive analyses there are also "micro-analytical techniques", which examine a microscopic part of the object by destroying a small part of the object without causing any visual damage (Van Grieken and Janssen, 2005). In microanalysis the corresponding quantities are about 5 mg and 0.1 mL (Stuart, 2007). These techniques are useful when sampling from the object is strictly required but limited quantity of sample is available, for instance laser induced breakdown spectroscopy (LIBS) or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

Ideally, the use of techniques which can be directly applied on the artwork without any need for sampling are preferred in conservation (Cucci *et al.*, 2011). On the other hand, for an analytical procedure to be considered non-invasive, it requires not only that no samples are taken from the object analysed, but also that the object does not move from its normal location, which presents a risk of accidental damage (Sarrazin *et al.*, 2009). Besides, locations where the measurement must take place may not be readily accessible, and the cost of installing and maintaining multiple stationary instruments can be high (Down and Lehr, 2004). With the current development of the technology and computer science, it is possible to make use of portable equipment, whose size and weight allow to measure in situ, with no need for sampling or moving the object into a laboratory. For this, a range of mobile equipment has been developed and investigated over the last years (Anglos and Karidas, 2009; Picollo *et al.*, 2014) and is becoming common in conservation laboratories and museums (Shashoua, 2001; Chércoles Asensio *et al.,* 2009; Miliani *et al.,* 2006). This mobile equipment may include several analytical techniques such as X-ray radiography, XRF, multispectral imaging, portable NMR, FTIR or Raman spectroscopy. Some of the advantages of portable equipment over conventional instruments are for instance: they are smaller and lighter, they can be easily transported to any location, they can work off batteries and/or mains power, they

avoid the need for samplimg, they are simpler to use or they take less space in the laboratory. On the other hand, portable equipment is in general less sensitive than stationary ones (McMahon, 2007) and they can also be more expensive. Therefore, when considering the use of a portable or stationary instruments, several factors should be taken into account such as: cost, physical requirement and logistic involvement (Down and Lehr, 2004).

However, non-destructive techniques alone cannot always provide a sufficiently detailed characterization of the samples (Prati *et al.*, 2010). Since plastics are very complex materials that may include both organic and inorganic materials in their composition, different instrumental analytical techniques have to be used for the identification of both the polymers and the additives that compose plastics materials (Stuart, 2007). As detailed in Table 14, very diverse information related to plastics materials can be achieved through both non-destructive and destructive techniques. For the identification of the polymers, plasticizers, organic and polymeric degradation compounds and organic additives, techniques such as FTIR, Raman Spectroscopy or GC coupled to Mass spectroscopy may be used. On the other hand, inorganic compounds within plastics (fillers, pigments, organometallic stabilizers etc.) can be identified by means of XRD, XRF or SEM coupled with energy dispersive X-ray spectroscopy (EDX). Therefore, for a complete characterization of the polymer it is necessary the use of more than on analytical tool and to understand the basis of each analytical technique and the information that each one can proportionate.

In Fourier Transform Infrared Spectroscopy (FTIR) a spectrum is obtained by irradiating a sample with infrared region (λ = 1mm to 750 nm) and by measuring what fraction of the incident radiation is absorbed at a particular energy. IR radiation is absorbed most efficiently when its frequency matches almost exactly the frequency of internal motions within a molecule. For radiation with frequencies in the IR, relevant motions are the vibrations of atomic bonds within the molecules of inorganic and organic compounds (Varella, 2013).

In the case of plastics materials, both polymer and plasticizers can be identified by FT-IR, as well as the degradation of polymer and organic additives. In addition to qualitative analysis, quantitative measurements may be achieved by mean of this technique (Derrick *et al.*, 1999), which can be used for the quantification of plasticizer loss.

Table 14: Analytical methods for characterization of plastics.

	DSC	FTIR	FTIR RAMAN	(py) GC-MS	GPC	IC	SEM-EDX	TGA	XRD	XRF
Organic compounds	✓	✓	✓	✓	✓	✓	✗	✓	✗	✗
Inorganic compounds	✗	•	✓	✗	✗	✓	✓	✗	✓	✓
Polymer identification	✗	✓	✓	✓	✗	✗	✗	✗	✗	✗
Laminate identification	•	•	•	✓	✗	✗	✗	✗	✗	✗
Plasticizer identification	✗	✓	✓	✓	✗	✗	✗	✗	✗	✗
Inorganic filler identification	✗	•	✓	✗	✗	✗	✓	✗	✓	✓
Organic filler identification	✗	•	•	✓	✗	✗	✗	✗	✗	✗
Other organic additives	✗	•	•	✓	✗	✓	✗	✗	✗	✗
Other inorganic additives	✗	•	•	✗	✗	✓	✓	✗	✓	✓
Organic degradation products	✗	✓	✓	✓	✗	✓	✗	✗	✗	✗
Inorganic degradation products	✗	•	✓	✗	✗	✓	✓	✗	✓	✓
Gaseous degradation products	✗	✗	✗	✓	✗	✗	✗	✓	✗	✗
Polymer degradation	✓	✓	✓	✓	✓	✗	✗	•	✗	✗
Plasticizer loss	✗	✓	•	✓	✗	✗	✗	✓	✗	✗
Filler degradation	✗	✗	✗	✗	✗	✓	✓	✗	•	✓

Legend: Suitable ✓ Possible • Unsuitable ✗

While IR spectroscopy depends on a change in the permanent dipole moment of the chemical bond or molecule with the vibrational normal mode in order to produce absorption, Raman spectroscopy depends on a change in the induced dipole moment or polarization to produce Raman scattering. The more symmetric the molecule is, the greater the differences will be between the IR and Raman spectra (Koenig, 1999). By means of both techniques, complementary and valuable information can be obtained not only about the polymer composition but also on its conformation. IR spectral region of the electromagnetic spectrum includes radiation with wavenumbers ranging from about 14.000 to 20 cm^{-1}, divided in IR region into the near (NIR), middle (IR or mid-IR), and far (FIR) sub-regions (Derrick *et al.*, 1999). A popular IR-surface-analysis technique for polymers is Attenuated total reflectance (ATR) spectroscopy also called internal reflection spectroscopy (IRS) or multiple internal reflectance (MIR) spectroscopy (Scheirs, 2000). Based on the fact that internally reflected IR radiation will penetrate a short distance into a lower-refractive-index medium, a sample in optical contact with the surface of the IRS element will be exposed to IR radiation. The sample can then absorb the radiation and produce a spectrum. Only the surface of the sample is analyzed, since the beam penetrates just a few micrometers into the sample. Varying the angle of incidence can change the number of reflections and their position within the IRS element (Derrick *et al.*, 1999). The sample requirements for ATR spectroscopy is that the sample is smooth, planar and pliable in order to have an suitable contact between the ATR and the sample and avoid reduction of the intensity of the absorption bands at high frequencies due to a not optimum contact. Thus, ATR spectroscopy is particularly useful for polymers that are soft and can be readily pressed against the internal reflection crystal (Scheirs, 2000). Due to the fact that ATR spectroscopy is a surface analytical technique, it is ideal for detecting the contamination and degradation of a polymer surface (Scheirs, 2000).

Chromatography is the separation of molecular mixtures by distribution between two or more phases: a stationary phase being a two-dimensional phase (a surface) and a moving phase passing though the column containing the two-

dimensional phase. In Gas chromatography (GC) the stationary phase may be either liquid (gas-liquid chromatography) or solid (gas-solid chromatography) (Cheremisinoff, 1996) and the carrier gas is usually an inert gas (nitrogen or helium). The sample is usually injected at high temperature to ensure volatilization and is analyzed in this state, which could be a limitation. The analyte mixture is separated depending on the affinity of different compounds with the stationary phase. Thus, the higher the interaction with the stationary phase, the longer the time to be eluted, also called "retention time". Liquid chromatography (LC) relies on pumps to pass a pressurized liquid solvent containing the sample mixture through a column filled with a solid adsorbent material. (Snyder *et al.*, 2009) Actually, Mass spectroscopy (MS) coupled to both separation techniques, GC and LC, is one of the detection systems allowing the separated components of the mixture to be analyzed, by measuring the mass-to-charge ratio and abundance of gas-phase ions. When analyzing plastics, the hyphenation with MS can be used for the identification of mixtures of polymers, plasticizers, degradation products and organic additives in the plastics (Quye and Williamson, 1999; Hanton, 2001). Gel permeation (GPC), also called size exclusion chromatography (SEC) and Ion chromatography (IC) are the two configurations of LC that are actually most used in the characterization of polymers. By means of GPC, molecules in solution pass through columns packed with very small, round, porous particles and get separated in their way through. Thus, GPC, is used to determine the average molecular weight distribution of a polymer sample, as well as it can help to obtain qualitative information on long chain branching or determine the composition distribution of copolymers (Cheremisinoff, 1996). IC is a chromatographic method of separation of ions, performed on a column packed with a solid-exchange material to determine inorganic and small organic ions, as well as larger organic anions and cations (Fritz and Gjerde, 2009). IC is based on the interaction between the molecules being eluted through the column and the solid support in the column. The stronger is the ionic interaction (based on the difference of charges between the column and the sample molecules) the higher is the retention on the chromatographic column.

Diffraction effects are observed when electromagnetic radiation impinges on periodic structures with geometrical variations on the length scale of the wavelength of the radiation (Birkholz, 2005). Thus, when electromagnetic or corpuscular radiation is diffracted by matter, a scattering diagram or diffraction pattern is produced (Günzler and William, 2001). Since X-ray diffraction (XRD) analyses generally deals with crystalline matter (either single crystals or crystalline powders), inorganic compounds deposited on plastic surface, such as fillers, salts, crystalline degradation product etc., can be detected by means of this technique (Quye and Williamson, 1999). In the case of polymers crystals the diffraction patterns is due to the fact that molecules, in this case polymer chains, rather than atoms, conform the lattice points of the unit cells (Mitchell, 2004). In semicrystalline polymers, which are generally described as consisting of a crystalline phase and an amorphous phase, the crystalline phase can be determined by XRD (Chung and Smith, 2000). The Crystalline Index is a relative measure of the crystallinity: CI=*Aa* 100/(*Ac*+*Aa*) where *Ac* is the area of the crystalline peaks, *Aa* the area under the amorphous peaks and (*Ac*+*Aa*) is the total scattered intensity (Smith, 1999).

Energy dispersive X-ray (EDX) and X-ray fluorescence (XRF) techniques are used for the identification of inorganic fillers, pigments and inorganic degradation products in plastics materials (Quye and Williamson, 1999). Both techniques, EDX and XRF, are based in the same principles: the sample is hit with an irradiation (an electron beam in EDX and a high-energy X-ray beam in XRF), creating an electron vacancy, which is refilled by an electron from higher energy orbitals, and releasing energy (Dieing *et al.*, 2011). Secondary X-rays with a specific and constant energy that is unique for each element are released.

Other techniques used to characterize plastics materials are Differential Scanning Calorimetry (DSC), and Thermo Gravimetric Analysis (TGA). DSC is a technique where the difference in energy input to a sample and a reference material is measured while the sample and reference are subjected to a controlled temperature program (Cheremisinoff, 1996). The temperature and heat flow

associated with the sample´s transitions as a function of time and temperature are recorded. These measurements provide qualitative and quantitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity such as glass transition, melting and crystallisation (Varella, 2013). In polymers, the primary use of DSC analyses is the detection and quantification of the crystalline melting process and the calculation of the degree of crystallinity for a polymer (Sepe, 1997). On the other hand, TGA analysis measures the amount and rate of weight changes in a material as a function of temperature or time (Sepe, 1997). By means of this technique, the quantification of plasticiser loss, filler loss, weight % filler etc. can be determined.

Nuclear magnetic resonance spectroscopy (NMR), is a technique that is used for the structure determination of unknown samples based on the magnetic properties of atomic nuclei (Günther, 2013). The frequency of absorption for a nucleus of interest relative to the frequency of absorption of a molecular standard is called the chemical shift of the nucleus (Ghosal and Srivastava, 2009). Since the chemical environment affects the magnetic properties of the measured atomic nuclei, identical atoms or functional groups will give different NMR signal ("chemical shift") according to the adjacent substituents, providing information about the structure of the molecule. ^{13}C NMR and ^{1}H NMR spectra are the most used in chemistry and biochemistry, even though, ^{19}F, ^{14}N and ^{31}P nuclei also provide valuable information (Günther, 2013). In the case of polymers, NMR provides qualitative and quantitative analyses, although the applicability of NMR spectroscopy extends even beyond chemical characterization, to the investigation of physical phenomena such as kinetics, dynamics and morphology (Brandolini and Hills, 2000).

1.4.1 Analysis and characterization of PVC

Like any other plastic, the identification of PVC should be carried out following a systematic approach: preliminary tests, detection of elements, determination of characteristic values, and, finally, specific analytical techniques. For an exact identification, however, the test sample should first be purified to remove additives (plasticizers, fillers, pigments, etc.) that may affect the results of an analysis (Chanda and Roy, 2006). In the case of PVC polymers, purification may be achieved by extraction of plasticizer and additives from the polymer blend, for instance by means of di-isopropyl ether (Shashoua, 2001).

A specific test for chlorine containing polymers, like PVC, is the Beilstein test, which consists on the identification of the color of a small piece of test material on a copper wire heated over a Bunsen burner (Williams, 2000). The presence of halogens (chlorine, bromine, iodine) is detected by the green color produced as a consequence of the copper halide volatilization. In unplasticized PVC the hydrochloric acid smell will be noticeable, while the plasticizer smell will be evident when burning plasticized PVC (Patrick, 2005). Another test for the identification of poly (vinyl chloride) is the boiling of their pyridine solutions with a few drops of methanolic sodium hydroxide (5%). In a positive test, a brown coloration and eventually dark brown precipitates is formed (Chanda and Roy, 2006). Density can be also utilized in water flotation testing to determine if it sinks, however other polymers as acrylonitrile-butadiene-styrene and polycarbonate have similar densities (Patrick, 2005).

To obtain more accurate and sensitive analyses chromatographic techniques such as GC or LC have to be used. However, the application of gas chromatography to polymers is restricted due to their high molecular mass and low volatility (Haken, 1998) and the need for pyrolysis of the sample. Pyrolysis consists of heating the sample until it degrades and releases low molecular mass fragments (Seidel, 2008), which then can be separated chromatographically and identified by mass

spectrometry. By means of highly sensitive GC-MS it is possible to separate and identify the plasticizer within the PVC polymer, as well as the presence and amount of low molecular weight species in a resin or vinyl compound (Shashoua, 2001; Seidel, 2008).

The NMR technique has been broadly used for the analysis of polymers, providing information on molecular structure, dynamics of the chain, crystallinity, network formation and chain entanglement (Seidel, 2008). In the particular case of PVC, studies with this technique have shown the presence of important ordered regions within the PVC chain, ultimately forming the microcrystalline regions (Wilkes *et al.*, 2005).

Identification of the type of functional groups present in a polymer is effectively achieved by spectroscopic methods like FTIR, ATR) and Raman Spectroscopy. PVC in particular, has been studied frequently with FTIR spectroscopy because its IR spectrum contains exhaustive information about the configurational and conformational content of the sample (Koenig, 1999). Thus, FTIR spectroscopy has been widely employed to determine the important chemical features of the PVC molecule, including determinations of the polymer's tacticity (Wilkes *et al.*, 2005), while ATR-FTIR allows the surface of PVC films to be explored (Seidel, 2008). Not only the infrared bands corresponding to PVC can be identified, but also those coming from the additive joining the PVC polymer. Typical infrared peaks of PVC polymer in absence of additives and some common additives are shown in Table 15 (Wilkes *et al.*, 2005; Tabb and Koenig, 1975).

As mentioned before, IR depends on a change in the permanent dipole moment of the chemical bond or molecule, while Raman depends on a change in the induced dipole moment or polarization and when combining both techniques it is possible to obtain comprehensive information about polymers conformation. In the particular case of the PVC polymer, the amorphous and crystalline structure can be distinguished by means of these techniques (Wypych, 2008), as well as two

syndiotactic conformational structures (extended and folded) have been detected (Koenig, 1999) Furthermore, Resonance Raman Spectroscopy is an additional spectroscopic technique used for the investigation of molecular structures.

Table 15: Infrared Spectroscopy peaks of PVC and additives.

Peak Assignment	**Wavenumber (cm^{-1})**
Aliphatic CH_2 and C-H stretching (PVC)	2971, 2911
CH_2 bending (wag) (PVC)	1435 (amorphous), 1427 (crystalline)
C-H in CHCl (PVC)	1330
C-H in CHCl (PVC)	1254
C-C stretching (PVC)	1098
CH_2 rocking (PVC)	967
C-Cl stretching (PVC)	693
C-Cl stretching (PVC)	616 (amorphous), 636 (crystalline)
TiO_2	500-1000 (Broadening)
$CaCO_3$	876
Acrylic impact or flow modifier	1733-1734
styrene/acrylonitrile (SAN) flow modifier	2238
Plasticizer (C=O)	1726
Plasticizer (CH stretching)	3000

The enhanced intensity spectrum takes place when the laser exciting frequency approaches that of an allowed electronic transition in the molecule being examined. Those normal modes that are vibronically active in the electronic transition exhibit a pronounced enhancement of their intensities by a factor as great as 10^4 or 10^5 (Bowe and Maddams, 1989) and are generally associated with the electronic chromophore being excited (Koenig, 1999). In the case of PVC, Resonance Raman Spectroscopy is used to evidence signs of degradation due to the formation of conjugated polyene sequences which act as chromophores.

For the chemical investigation of the PVC polymer and its additives, several techniques may be used. Near Infrared Spectroscopy (NIR), has been used to

analyse the composition of vinyl compounds and determine the identity and the level of mixtures of plasticizers in the formulations. Also, thermal methods based on the measurements of the polymer properties as a function of temperature or time at constant temperature (Seidel, 2008), e.g. DSC, have been used to characterize the glass transition of vinyl compounds and to determine the level of stability (Wilkes *et al.*, 2005).

1.4.2. Surface examination of PVC

The selection of appropriate techniques is an important aspect during the examination of a plastic surface, depending not only on the type of material under investigation, but also on the type of information to be achieved. A summary of some common techniques used for surface characterization of PVC and the information provided by each technique is shown in Table 16 (Stamm, 2008).

In X-ray photoelectron spectroscopy (XPS), a surface analytical technique based on the photoelectron effect, the sample surface is bombarded with mono-energetic low energy (X-ray photons) (Bart, 2006) resulting in the emission of a core level electron (photoelectron). The binding energy of the electron is the parameter which identifies the electron specifically, both in terms of its parent element and atomic energy level and the X-ray induced photoelectron spectrum is the graph of the photoelectron intensity versus electron energy. (Watts and Wolstenholme, 2003). Since none of the elements share the same set of electronic binding energies, measurement of the photoelectron kinetic energies provides elemental analysis (Günzle and William, 2001). Most polymeric systems can be successfully examined in a conventional XPS. However, some disadvantages of XPS techniques are, for instance, the use of expensive equipment, some radiation damage to X-ray sensitive materials or poor depth resolution (Bart, 2006).

Table 16: Common techniques used for surface characterization.

Technique	Probe In / out	Smallest information depth / width (nm)	Information	Comments
X-Ray photoelectron spectroscopy XPS	X-Rays / electrons	5 / 3000	Chemical composition, binding state	Quantitative, vacuum technique, lateral imaging possible
Scanning force microscopy (SFM) or Atomic force microscopy (AFM)	Cantilever	0.05 / 1	Surface topography, composition, toughness	Atomic resolution, many different modes
Electron microscopy	Electrons	2/1	Surface topography	Vacuum technique
Optical microscopy OM	Light	0.1/300	Surface roughness, structure	Many possibilities, good height resolution with interference techniques

Optical Microscopy (OM) or Light Microscopy uses visible light and a system of lenses to magnify images of small samples. An ordinary light microscope is not well-suited for studying the 3D structure of a specimen. It presents a 2D image consisting of a superposition of in-focus and out-of-focus regions of the specimen. For this, confocal microscopy is a method developed to prevent out-of-focus light from reaching the detector (Bart, 2006). Light microscopy may work in transmission mode, where the radiation passes through the specimen and is collected on the other side, requiring a thin specimen or in reflection mode where the light is collected from the surface it arrives at, allowing thicker specimens (Sawyer *et al.*, 2008). Transmitted light microscopy reveals the internal structure of transparent material and may be used in the examination of individual fibres, particle morphology and orientation. It can also be used in the examination of thin sections of resinous coating. Reflected light microscopy is used to examine surface morphology. Rough

surfaces and those where gloss or transparency is not of major importance or opaque materials can be successfully examined using simple reflected light methods (Bart, 2006).

Within electron microscopy, there are two main techniques: Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). In general, SEM provide images of external morphology, rather similar in appearance to those formed by the human eye, while TEM probes the internal structure of solids and gives access to microstructural or ultra-structural details not familiar to the human eye (Goodhew *et al.*, 2000). Not only structural but also chemical information can be obtained by means of both SEM and TEM microscopy.

While OM produces magnified images by means of glass lenses and visible or ultra violet light, "electron microscopes" produce magnified images by the use of electrostatic or electromagnetic lenses with fast-moving electrons as illumination source, providing high or very high resolution (Watt, 1997). The first class of electron microscopy is based on a stationary beam incident along a fixed direction, such as conventional transmission electron microscopy (CTEM), while the second type is based of a fine electron probe scanned across the specimen, such as scanning transmission electron microscopy (STEM), scanning electron microscopy (SEM) or Auger Electron spectroscopy (AES)/scanning Auger microscopy (SAM). The stationary beam methods are based on image formation processes, whereas the scanning methods are essentially "mapping" techniques (Günzler and Williams, 2001).

Imaging formation in the SEM depends on the acquisition of signals produced from the electron beam and specimen interaction (Zhou and Wang, 2007). Within SEM, there are two types of methods to produce images: by the secondary electrons (produced when the primary beam hits the samples' surface and electrons are emitted from the atoms excited by the beam) and by backscattered electrons, which are incident electrons that are elastically scattered by the sample atom though and angle of more that 90º (Zhou and Wang, 2007).

When comparing electron microscopy with light microscopy, SEM and TEM have greater resolving capabilities, as well as a wider and higher magnification range than OM (Table 17, Flegler *et al.*, 1993). However, electron microscopes require operation under high – vacuum conditions, with the exception of Environmental Scanning Electron Microscopy (ESEM), and the examined samples often require more extensive preparation than that needed for OP.

Table 17: SEM, TEM and Optical Microscopy features

Feature	OP	TEM	SEM
General Use	Surface morphology and sections (1-40 μm)	Sections (40-150 nm) or small particles on thin membranes	Surface morphology
Source Illumination	Visible Light	High-speed electrons	High-speed electrons
Best Resolution	ca. 200 nm	ca. 0.2 nm	ca. 3-6 nm
Magnification Range	10-1,000x	500-500,000x	20-15,000x
Depth of field	0.002-0.05 nm (N.A. 1.5)	0.004-0.006 mm (N.A. 10^{-3})	0.0031 mm
Lens Type	Glass	Electromagnetic	Electromagnetic
Image ray-formation spot	On eye by lenses	On phosphorescent plate by lenses	On cathode tube by scanning device

On the other hand, Atomic Force Microscopy technique can resolve individual atoms and can operate at atmospheric pressure or even under water, as well as it does not require specimen preparation beyond the creation or exposure of a surface of interest (Sawyer *et al.*, 2008). In AFM, the probe consists of a sharp tip grown on the underside of a flexible beam called *cantilever* (Seidel, 2008). AFM works by bringing the *cantilever* tip in contact with the surface to be imagined. An ionic repulsive force from the surface applied to the tip bends the *cantilever* upwards. A topographic image of the sample is obtained by plotting the deflection of the cantilever versus its position on the sample (Butt *et al.*, 2005). Another characteristic of AFM microscopes is that they have no lenses and build up their images point by point (Sawyer *et al.*, 2008).

Even though OM, SEM, TEM and AFM have been used for polymer surface characterization, very different resolution ranges are provided by them (Table 18, Sawyer *et al.*, 2008).

Table 18: SEM, AFM and Optical Microscopy size ranges

Technique	Size ranges
Optical Microscopy (OM)	200nm – 200μm
Scanning Electron Microscopy (SEM)	4nm - 4mm
Transmission Electron Microscopy (TEM)	0, 2nm – 0, 2mm
Atomic Force Microcopy (AFM)	0, 2nm – 0, 2mm

In addition, it must be considered that contrary to optical microscopy and scanning probe microscopies (e.g. AFM), electron microscopy radiation often changes the polymer during imaging, which can affect the interpretation of the image. However, each technique has its own benefits that must be understood (Sawyer *et al.*, 2008).

Unlike optical microscopy, Confocal Profilometry has the capability of creating a bright image of the in-focus region of the specimen, providing 3D images from rough and uneven surfaces. Profilometer is essentially a confocal microscope that obtains a high number of images at different focal heights on the surface topography and creates a 3D image (Hamilton and Wilson, 1982; Lange et al., 1993). It "optically" sections the surface and a computer transforms a series of sections into digital images and a topographic map (Lange *et al.*, 1993). A confocal microscope works by geometrically matching two conjugate focal points in image space. When the two points, a point source and a point detector, are well matched, satisfying the confocal condition, the point source will be imaged to the detector with maximal intensity. If the points are not well matched and are displaced from the focus locations, the point detector rejects the broadened scattered light and detects a lower intensity (Cha *et al.*, 2000). Additional 'stitching' of several scans from adjoining surface areas may be

created from the profilometric images, enabling the examination of much broader areas than with SEM or AFM. In could be said that confocal profilometry complements SEM imaging and overcomes depth of field limitations of optical microscopy (van den Berg *et al.*, 2008). In Table 19 (Malacara, 2007)., a summary of differences between AFM, Scanning Tunnelling Microscopy (STM), White Light Interferometric Optical Profiler and Confocal Microscope is given (Malacara, 2007).

Table 19: The main characteristic parameters of a STM, White Light Interferometric Optical Profilometer, and Confocal Microscope.

	AFM/STM	**White light interferometric**	**Confocal microscopy**
X, Y resolution	2-10 nm AFM 0.1 nm STM	0.5 μm (NA objective dependent)	0.5 μm (NA objective and lateral sampling dependent)
Z resolution	0.1 nm AFM 0.01 nm STM	0.3 nm	1-20 nm (Dependent on objective magnification)
Field of view	70-150 μm	100 x 100 μm to 10 x 10 mm but can be extended by stitching	100 x 100 μm to 10 x 10 mm but can be extended by increasing lateral sampling lens array objective
Measurable height range	Up to 20 μm	8 mm (or limited by working distance of objective)	Limited by working distance of objective
Sample preparation	Minimal	None	None
Contact with the sample	Optional	No	No
Special surface requirements	STM-only conductive surfaces	Needs correction for dissimilar materials and film coatings	Needs correction for dissimilar materials and film coatings
Scanning	Point by point	Full field of view	Point by point

Full field dynamic motion of sample measurement	No	Yes	No
Through the glass measurement	Not possible	Possible	Possible
Film thickness	Only if film has a step	Minimum 0.1 μm	Minimum 1 μm
Measurable optical properties of surface film	Indirectly through correlation with topography	Yes	Yes
Other measurable material	Numerous: adhesive, electric, magnetic, visco-elastic, elastic etc.	No	No

Among the techniques used for surface examination above described, SEM, OM and AFM have been more widely applied to the characterization of the PVC (Kuisma, 2006). SEM, for instance, has revealed important features in the particulate morphology of suspension, mass and dispersion polymers of PVC, while OM has been used to determine the relative porosity of suspension PVC particles, making use of dedicated imagine analysis software (Wilkes *et al.*, 2005).

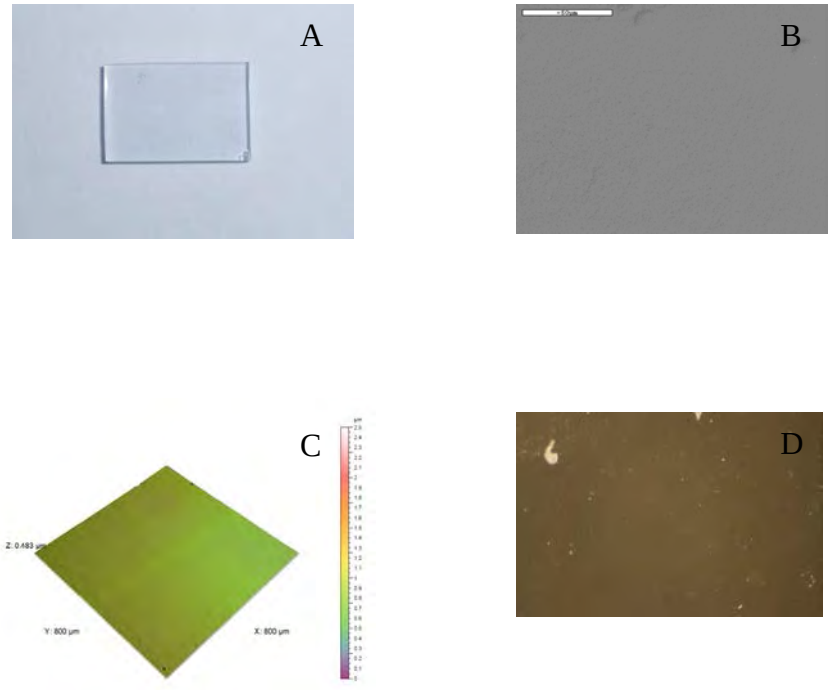


Figure 13: Plasticized PVC (A) to the naked eye, (B) characterized by SEM, (C) Profilometry and (D) Optical Microscopy

Moreover, AFM has been used in numerous studies as a technique for the surface characterization of PVC (Kuisma *et al.*, 2005), providing high-resolution images and the relevant information relative to the adsorption, adhesion and other surface-dominated phenomena that provides (Seidel, 2008). Further information about surface topography can be obtained by means of profilometry (Wilson, 1995), which provides not only 2D and 3D images, but also roughness parameters used for full characterization of the surface topography (Figure 13).

1.4.3. Analytical techniques for the examination and quantification of the cleaning

In the industry, cleanliness verification is done by means of instrumental methods that range from inexpensive techniques, such as contact angle measurements or particle counts (Määttä et al. 2007), to expensive ones, which also provide cleanliness quantification and the chemical composition of the contaminant, like FTIR, SEM/EDX or X-Ray Photoelectron Spectroscopy (XPS) (Kuisma *et al.*, 2005, Kanegsberg and Kanegsberg, 2000). In the case of an artwork, cleaning must be risk-free and guarantee no damages to the surface. Thus, the surface has to be examined after the cleaning in order to verify not only the cleanliness but also the suitability of the cleaning method in terms of safety for the artwork.

For the examination of artworks 'surfaces after cleaning treatments, techniques such as observation by the naked eye or common surface examination techniques such as, OM, SEM-EDX, AFM, Light Interferometry or Confocal Profilometry have been used for the physical and visual examination of the surface (Fairbrass, 1999; Huys and van Oosten, 2005; Gaspar *et al.*, 2003; van den Berg *et al.*, 2008; Ioanid *et al.*, 2011). Among them, the naked eye provides direct information about the surface (Stout and Blunt, 2000) and it is still a common method of assessment (Gaspar *et al.*, 2003). However, the level of detail provided is often not sufficient for a reliable evaluation of the cleaning effects. Thus, for more accurate information about the cleaning, 2D and/or 3D images can be obtained by means of other techniques as previously described. Furthermore, changes in gloss and colour are often used to determine the impact of cleaning treatments on cleaned surfaces.

In the case of plastic artworks, examination methods commonly used for the assessment of the cleaning effects and the investigation of changes produced on the plastics surfaces include OM (Huys and van Oosten, 2005; Fairbrass, 1999) and Gloss Measurement (Shashoua, 2011). As general, gloss may be defined as the ability of a surface to reflect specular light. Materials with smooth surfaces, such as plastics,

appear highly reflective (glossy), while very rough surfaces reflect no specular light and therefore appear matt. When cleaning plastics, damages such as scratches, melting of the surface or lost of additives may occur, leading to changes of the surface's appearance in terms of gloss. By taking an initial measurement, every value recorded afterward can be compared to the initial numerical value to assess how much of the gloss layer has been lost. The loss of gloss can be crucial to the artwork's appearance or presentation, in addition to the preservation For gloss determination, a gloss meter is used in accordance with ASTM D523. Light is reflected from the surface into a detector at a 20°, 60° or 85° angle, depending on the reflectance of the surface (Lampman, 2003).

Aspects more related to museum environments, such as sampling limitations or mobility of the instrumental technique, play also a significant role during the cleaning examination. As above described, techniques that require sampling from the material, such as SEM or ATM, become more restrictive in their use than those that may be directly applied on the artwork with no material subtraction, such as optical microscopy, or profilometry.

Furthermore, analytical techniques have been used for the chemical investigation of artworks' surface after cleaning treatments, for example FTIR (Ioanid *et al.*, 2011), or the investigation of pollutants' removal and the presence of residues by means of techniques like EDX-ray spectroscopy (Gaspar et al., 2003). Apart from examination, any cleaning process necessarily involves the quantification of the cleaning in terms of efficiency. Cleanliness can be determined by analysing a representative sample with chosen analytical techniques, from data collected over a period of time and compared with the performance of samples as final products (Kanegsberg and Kanegsberg, 2000). Moreover, the comparison between cleaning treatments is based upon key parameters associated with cleaning surfaces (Gaspar *et al.*, 2003). In conservation, even though the naked eye is generally used to evaluate the cleaning efficiency by means of the human visual perception usual parameters measured to determine and quantify the cleanliness level are colour,

brightness and contact angle (Shashoua *et al.*, 2011, Levédrine *et al.*, 2012).

The CIELAB system (CIE 1976 L*a*b*) was proposed to quantify spectral power distributions, which would be perceived as uniform colour by means of the CIELAB coordinates (L*a*b*). While L* stands for a lightness component closely matching human perception, a* and b* are colour opponent dimensions (CIE 15: 2004). The amount and the sign of the so-called colour differences ΔL*, Δa*, Δb* are expressed as (Kang, 2006).

ΔL^* { > 0 = Light; < 0 = Dark

Δa^* { > 0 = Redder; < 0 = Greener

Δb^* { > 0 = Yellower; < 0 = Bluer

CIELAB coordinates are calculated from tristimulus values; therefore the illuminant-observer conditions must be specified (Berger-Schun, 1994) during the measurement. The colour difference is calculated with a standardized formula, which enables to indicate quantitatively the approximate value of the perceived colour difference between two given colours (Klein, 2010):

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Additionally, relative indices calculated from the means of the L* values of a sample have been also provided for the quantification of the cleaning in industrial flooring applications (Redsven *et al.*, 2003) and it can be used as a tool for the comparison of the results obtained from different cleaning methods:

$$\text{Cleaning Index } (\%) = \frac{(L^*_{cleaned} - L^*_{soiled})}{(L^*_{unsoiled} - L^*_{soiled})} \times 100$$

In this formula, the higher is the Cleaning Index value, the more efficient is the cleaning method used. As previously mentioned, the contact angle has been also used in conservation to quantify the cleaning on plastics surfaces. The contact angle θ may be defined as a function of the wettability of the solid by that liquid. An angle approaching zero means that the liquid has spread and totally wet the surface (Brass, 1999), while a contact angle greater than 90° indicate poorly wetting liquids that do not spread on the plastic surface and are unlikely to result in adhesion (Shashoua, 2008). Contact angles measurements used to quantify cleaning are based on changes in surface energies induced by cleaning, due to residues from cleaning agents, surface damages such as scratches etc. (Shashoua *et al.*, 2011).

2. SCOPE AND AIMS

2.1 Aims of the research

Following the previous introduction, the scope of the present research was to investigate the cleaning of new and degraded plasticized PVC surfaces in order to find a reproducible methodology of study applied to the cleaning of plastics objects. The following goals were targeted to achieve this purpose:

1) Development of a methodology of study applicable to plastics artworks cleaning;
2) Finding of new effective and harmless cleaning methods specific for plasticized PVC material in both non-degraded and degraded stages
3) Finding of new methods to quantify the effectiveness of cleaning methods on plastics materials and testing on plasticized PVC;
4) Application of the obtained cleaning and quantification methods on real PVC objects

Furthermore, other minor objectives aimed during this investigation were:

1) Investigation of cleaning methods on commercialized plasticized PVC material instead of on laboratory made plasticized PVC samples;
2) Testing of commercialized dry cleaning methods for plastics materials on plasticized PVC;
3) Investigation of degradation mechanisms of the commercial plasticized PVC samples used in the present research.

2.2 Scope and thesis organization

The structure of the thesis was established following the aims described on section 2.1. For this, the selection of a plastic material common in museums and art collections was the first step in the methodology. Plasticized PVC, what is a common plastic in museum objects, was proposed as testing material. Instead of custom-made PVC samples, a commercialized PVC was used for the experiments, preventing from unrealistic situations in museums and art collections, where the composition of the plastics objects is often unknown or not fully identified. Thus, a commercial and uncoloured flexible PVC from Danish manufacturer VINK was used in the experimental part of this research.

Based on the concept of "cleaning", it became clear the necessity of including not only unsoiled samples but also samples in different stages of dirtiness. Thus, samples from the commercial PVC were naturally soiled and used as testing material during the cleaning. On the other hand, another mayor issue to consider when cleaning plastics objects is the degradation of the material. Among the factors that cause the degradation of PVC, temperature and photo-degradation are the more important. For this research, photo-degradation was considered the most likely factor affecting the PVC, since temperature is usually monitored and controlled within museums and art collections. Therefore, samples from the commercial PVC were artificially degraded and used for the cleaning investigation.

The next step in the methodology was the selection of cleaning techniques for the plasticized PVC samples. For this, a careful review of specialized literature in plastics cleaning and a comprehensive investigation about cleaning agents suitable for plasticized PVC was performed. The selected cleaning agents included organic and aqueous solutions in different proportions, detergents, commercial cleaners and dry cloths agents. This selection meant to be not only a review and testing of cleaning methods already proposed in conservation for plastics cleaning, but also the investigation of new cleaning methods specific for plasticized PVC.

Additionally, examination and analytical techniques were selected for the investigation of the cleaning results. Following the conservation criteria, all the selected techniques were non-destructive, as well as they were applied under ambient temperature and pressure lab conditions, guarantying a safe use on art objects. Since cleaning is in general a "superficial" action, techniques that provided information from the surface were selected for the examination different cleanings processes. Therefore, chemical variations occurred on the samples surface as a consequence of the cleanings were identified and investigated by means of ATR-FTIR spectroscopy, taking advantage of the few microns penetration in the surface of this technique and the possibility of application directly on the object with no need of sampling. On the other hand, physical modifications and colour changes were identified by non-destructive techniques traditionally used in conservation: optical microscopy and colorimetry, while non-contact profilometry technique was proposed for the examination of irregular surfaces and 3D objects.

Apart from the physical and chemical evaluation of the cleaning effects, the following step in the methodology was the quantification of the results obtained from the different cleanings in order to evaluate the efficiency. For this, traditional measurement of colour difference before and after the cleaning (largely used in conservation for the quantification of cleaning treatments), was proposed. However, due to the limitations of the quantification by colorimetric techniques when enough contrast between soiled and cleaned samples is not achieved or when samples do not a flat surface that allows the colorimetric analysis performance, alternative methods for the quantification were investigated in this research. Thus, topographical changes associated with the cleaning effects were proposed in order to find a new quantification method suitable for any PVC object.

As a closing stage of this research, the results obtained during the investigation of the commercial plasticized PVC cleaning were tested on a real PVC object. For this, an old doll composed of plasticized PVC and showing clear signs of degradation was cleaned following the methodology previously proposed.

3. A SURVEY FOR NECESSITY OF PLASTICS CLEANING IN THE MUSEUM ENVIRONMENT

With the purpose of enlarging the current knowledge on plastics cleaning in the conservation field, a survey within the Statens Museum for Kunst (SMK) in Copenhagen was performed in 2007, as a preliminary stage of this research and as part of the European Marie Curie program "EPISCON Project". In this survey, several plastics artworks from the SMK museum collection, all of them displayed indoors, were selected (Figure 14).

Figure 14: "Light Conductor" by artist Oivind Nygård.

The selected artworks were chosen to cover a wide range of plastics materials such as polyesters, acrylic resins, plasticized PVC and polyurethane. Dirt from the artworks' surfaces was examined following the procedure described on "A Dust Atlas" by Jacobsen and Ryhl-Svendsen (Jacobsen and Ryhl-Svendsen, 2004).

Following this methodology, samples of dirt were taken from the artworks' surfaces by means of pieces of sticky gelatine film attached at random to the objects' surfaces and then stripped off. As described by Yoon and Brimblecombe (Hun Yoon and Brimblecombe, 2001b) the advantages of this sticky film are: 1) it is inexpensive; 2) it is an easy and reproducible method; 3) it is an efficient collection method; 4) it has a wide application (applicable for measuring particulate matter using SEM or

image analysis) and 5) it is unobtrusive. After the gelatine films were detached from the objects, the particles on the gel were qualitatively analysed by optical microscopy in order to understand both the extent and the type of dirt that had settled on the artworks' surfaces.

In general, several types of dirt may be found on museum objects, whether exposed to outdoor or indoor conditions, such as chemical pollutants (ammonia, carboxylic acids etc.), skin flakes, fibres, sand, etc. Their sources can be the air conditioning and heating systems, visitors' clothing, exhibition materials, etc. could be observed. When observing the sticky gel strips detached from some plastics artworks at the SMK Museum under the optical microscope at 50x magnifications and bright illumination, many of these particles were identified, as shown in the following micrographs (Figure 15).

As result of the survey, it was concluded that all the examined materials exhibited dirt on the surface to a certain extent, regardless of the composition or conservation state of the artwork. Cleaning, therefore, seemed to be a necessary process, which level of significance depended on each particular object. Consequently, a comprehensive investigation into the cleaning of plastics objects in museum and art collections was required in order to define suitable cleaning methods for plastics objects.

ARTWORK 1

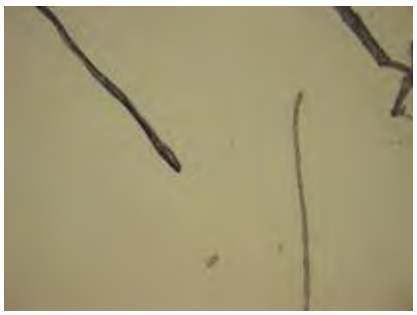
Composition: Plexiglas (PMM, poly methyl methacrylate)

Conservation State: Good. No degradation observed.

Cleaning state:

1mm

Skin flake



Fibres

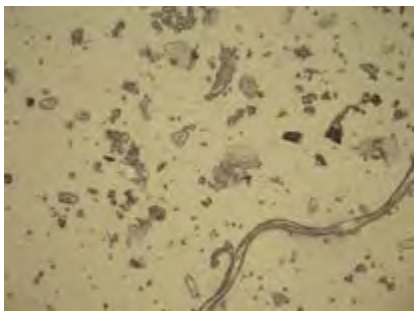
ARTWORK 2

Composition: Polyester

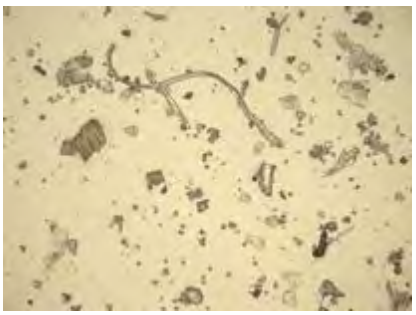
Conservation State: Good. No degradation observed.

Cleaning state:

1mm



Fibres, skin flakes, black and orange particles



Fibres, skin flakes, black and orange particles

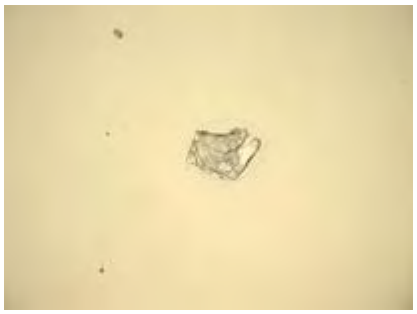
ARTWORK 3

Composition: Polyester

Conservation State: Some scratches on the surface. No degradation observed.

Cleaning state:

1mm



Skin flake

Fibres

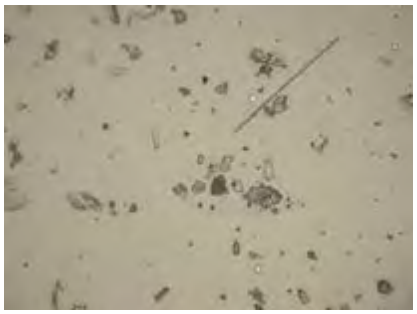
ARTWORK 4

Composition: Acrylic

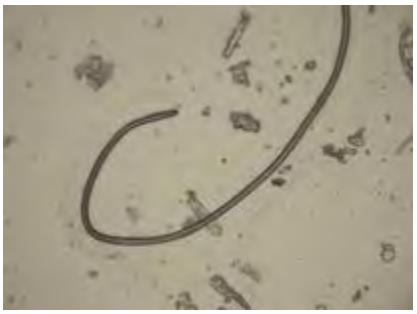
Conservation State: Light yellowing of some areas

Cleaning state:

1mm



Fibres, skin flakes and particles



Skin flakes, salt and fibres

ARTWORK 5

Composition: Plasticized PVC

Conservation State: Deformation and slight weakening in certain areas. No degradation observed.

Cleaning state:

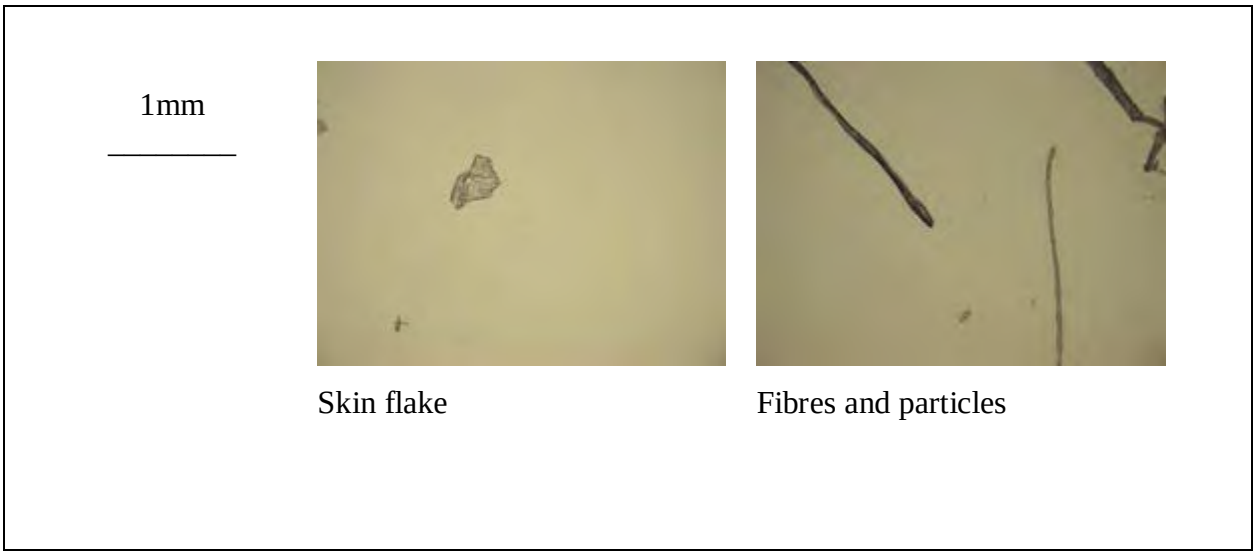


Figure 15: Micrographs from plastics' dirt samples under the optical microscope.

3.1. Study Design

The methodology proposed in this research was targeted on the study of cleaning plastic materials, in order to find innocuous and effective cleaning methods for plastics artworks (see chart described in Figure 16). Furthermore, the steps below described were applied to the particular case of plasticized PVC in an attempt to demonstrate the suitability of this methodology and find specific cleaning methods for this material.

Following the methodology developed in Figure 16, the first step was the selection of the plastic material. Then, a comprehensive chemical, physical and topographical examination was carried out in order to determinate the chemical composition and the physical and topographical characteristics of the material. Additionally, the selected plastic material was exposed to photo ageing and soling treatments to obtain degraded and soiled samples for the cleaning investigation. Afterwards, several cleaning methods were specifically proposed and tested on the samples (raw, aged and soiled). Finally, the cleaning results were quantified and assessed in terms of suitability and efficiency. The outcome of having followed this

methodology was the establishment of several conclusions on optimum cleaning agents and conditions for PVC applicable to artworks from museum collections.

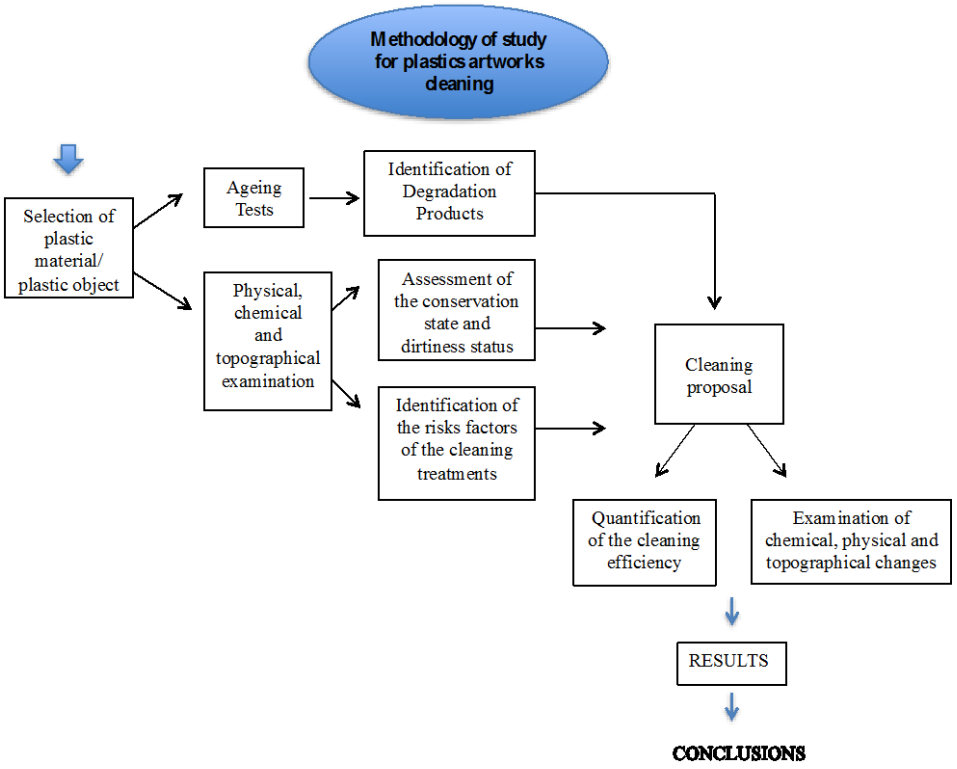


Figure 16: Study Design

4- PRELIMINARY STUDIES

4.1. Instrumental

For the investigation, the following analytical techniques were used:

- **Optical Microscopy.** Samples were observed under an Axiotech 100HD optical microscope. Micrographs were taken at several magnifications with both Dark and Bright Field illumination.

- **ATR-FTIR spectroscopy** was carried out with a Spectrum One FTIR Spectrometer (PerkinElmer) with a Diamond/ZnSe crystal and at 458° angle of incidence. 20 scans were recorded for each spectrum in the 4000–550 cm^{-1} range in absorbance mode at either 8 or 4 cm^{-1} resolution. No corrections were applied to the spectra after their collection.

- **GC-MS** was performed on a Varian 3400 gas chromatograph interfaced to a Saturn II or a Saturn 4D ion trap mass spectrometer (Analytical, Denmark). 1μL samples were injected manually using a micro syringe, and introduced in split mode (approximately 1:50) or alternatively splitless mode at a temperature of 250ºC. The temperature of the transfer line (GC to MS) and the manifold of the mass spectrometer were 250ºC and 200ºC, respectively. For the separation of the compounds, a polar column 0.32 mm i.d. x 30 m WCOT (wall coated open tubular) fused silica column coated with VF-23ms or alternatively with CP-SIL 8CB at a thickness of 0.25 μm (Analytical, Denmark) were used. Separation of a wide range of products was achieved using a temperature program from 50ºC to 300ºC. Full mass spectra were recorded every 0.5 s (mass range m/z 41-m/z 450 or m/z 50-m/z 425) and the compounds were identified using the NIST search engine (Agilent, Denmark).

- **X-ray fluorescence** was measured with a Philips PW 2400 Sequential XRF Spectrometer and evaluated by software UniQuant ver. 5.49. Detection limits were estimated to be 0.001-0.002 %. Calibration was performed using the pure elements. These analyses were carried out at the Danish Technological Institute.

- **UV-visible Spectroscopy** was carried out by means of an Ocean Optics USB4000 UV-Visible spectrometer with a Toshiba TCD1304AP 3648-element linear CCD-array detector.

- **Scanning Electron Microscopy (SEM)** was performed by means of a Jeol 5310-LV SEM, equipped with a Backscattered Electron Detector. This instrument is a low vacuum system, allowing for pressures ranging from 0 to 230 Pa and for working with unsputtered samples. For analysis, the system was running at about 25 Pa and at maximum 5kV accelerating voltage.

- **Non-contact profilometery** was carried out by means of two different equipments: an a μsurf Mobile (NanoFocus AG, Germany) equipped with a 20× objective, that measured 0.8 × 0.8 mm2 areas at a step width of 0.125 μm in the z-direction and an Usurf Explorer (NanoFocus AG, Germany), equipped with an 800 XS objective that measured 0.8 × 0.8 mm2 areas at a step widths of 0.03 mm and a 0.08 mm.

- **NMR spectroscopy:** Analysis was carried out on a 500 MHz Bruker Avance 2 NMR spectrometer. Both ^{1}H and ^{13}C spectra were recorded using a $CDCl_3$ or $CHCl_3$ solution with TMS as reference for chemical shifts. The DEPT spectrum recorded with a 135° flip angle was used for determination of the multiplicity of carbon substitution. The CO/CH_2 ratio was determined by integration of the ^{1}H spectrum.

- **LC-MS** was performed using a LCQ (Classic) MSn system (Finnigan, San Jose, CA, USA) equipped with an ESI (electrospray ionization) source and a complete TSP HPLC system (Thermo Separation Products Inc., San Jose, CA, USA). The HPLC system consists of a P4000 gradient high-pressure pump, a SCM vacuum degasser, an AS3000 auto-sampler and a UV6000LP PDA-detector. The LCQ system was operated in the normal mass mode (50-500 uma) with a maximum ion injection time of 200 ms. Only negative ions were assayed. Source parameters for negative ions: spray voltage -3.5 kV, heated capillary 200°C, sheath gas flow rate 80 (arb. units) and auxiliary gas flow rate 10 (arb. units). The chromatographic separation was carried out at ambient temperature using a Purospher RP-18e (125 x 4 mm, 5μm) column (Merck, Germany). The mobile phase (0,3 mL/min) was a gradient constructed from 100 % water (I) and 90 % acetonitrile v/v containing ammonium formate (40 mM) and formic acid (20 mM) (II) as follows (time, % II): 0, 5 %; 5, 5%; 20, 100%; 35, 100%; 40, 5%; 45, 5%. The samples were transferred into acetonitrile and 20 μL were injected. In addition samples were analyzed directly using the syringe-pump system. The semi-ester was dissolved (0.5 mg/mL) in a 40 % v/v acetonitrile containing ammonium formate (20 mM) and formic acid (10 mM).

- **X-ray Photoelectron Spectrometry (XPS)** of plasticized PVC samples were performed by a Thermo Scientific X-ray photoelectron spectrometer K-Alpha. Samples were mounted on a standard sample holder and analyzed using the micro focused, monochromatic Al Kα X-ray source, operated at room temperature and 5×10^{-9} mBar. The source worked at 200uA and 0.20 Kev in spots of 400μm. The software used was Avantage version 3.89. The size of the X-ray spot was chosen by the operator to match the sample and analysis type (spot sizes between 30 μm and 400 μm may be selected on K-Alpha.) K-Alpha's charge compensation system was employed during analyses. The analyses were carried out at the Danish Polymer Center, Denmark.

- **Color** was measured by means of a Colorimeter Minolta CM 2600D equipped with Standard Illuminant D65 light source (standardized daylight, 6500 K).

- **Gloss** was measured by means of a Minolta Multi-Gloss 268 Glossmeter with an illumination angle of 60º, as recommended for intermediate-gloss films (ASTM D2457-13).

4.2. Material Selection and Characterization

As previously mentioned, plasticized PVC is one of the most common plastics in museums and art collections. Many artworks created of "new" materials have used plasticized PVC, as it provides the creation process with a freedom not offered by traditional materials like stone or ceramic. In order to reproduce a real cleaning process in a museum or conservation centre, commercialized plasticized PVC was selected for the investigation, avoiding lab-made samples. The material chosen for this research was a plasticized PVC manufactured as a 2 mm thick and colorless sheet (product ref: 109200) by the company VINK (Denmark). As can be observed in Figure 17, the surface of this plasticized PVC was extremely smooth and even, which was a decisive feature for its selection as model material. The flat smooth surface allowed not only the detection of small variations on the surface topography occurred during the cleaning, but also the perfect contact with the ATR cell, necessary for the ATR-FTIR analyses used in the cleaning qualification and quantification. Furthermore, the manufacture of the material as a flat sheet made it appropriate for the weathering process and the physical and topographical analyses by means of the different techniques used in the research (such as colorimetry, non-contact profilometry or optical microscopy), as well as its flexibility and softness helped to its cutting into the specific sample sizes required for some of the analyses and examinations. From the chemical point of view, the homogeneous composition of the material enabled the quantification of the plasticizer and the identification of chemical changes during the cleaning process.

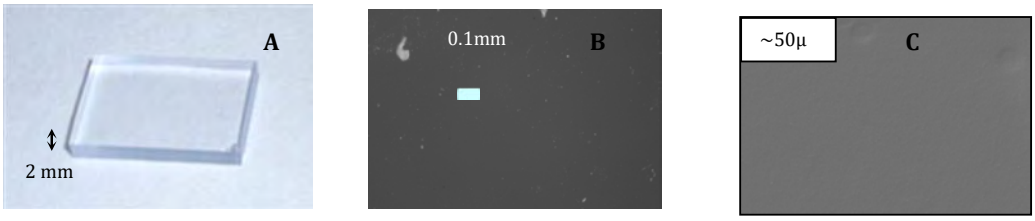


Figure 17: Plasticized PVC sample: (a) naked eye view, (b) view under optical microscopy and (c) view under SEM.

For the determination of the chemical composition of the commercial plasticized PVC, ATR-FTIR Spectroscopy, GC-MS, LC-MS, XPS and XFR were used. As can be observed in Figure 18, the ATR-FTIR spectrum of the plasticized PVC sheet perfectly matched with the general plasticized PVC ATR-FTIR spectrum, where the main bands of commercial PVC polymer and plasticizer were identified by comparison against reference spectra and the band assignments provided in the literature (Tabb and Koenig, 1975, Derrick *et al.,* 1999, Shashoua, 2008).

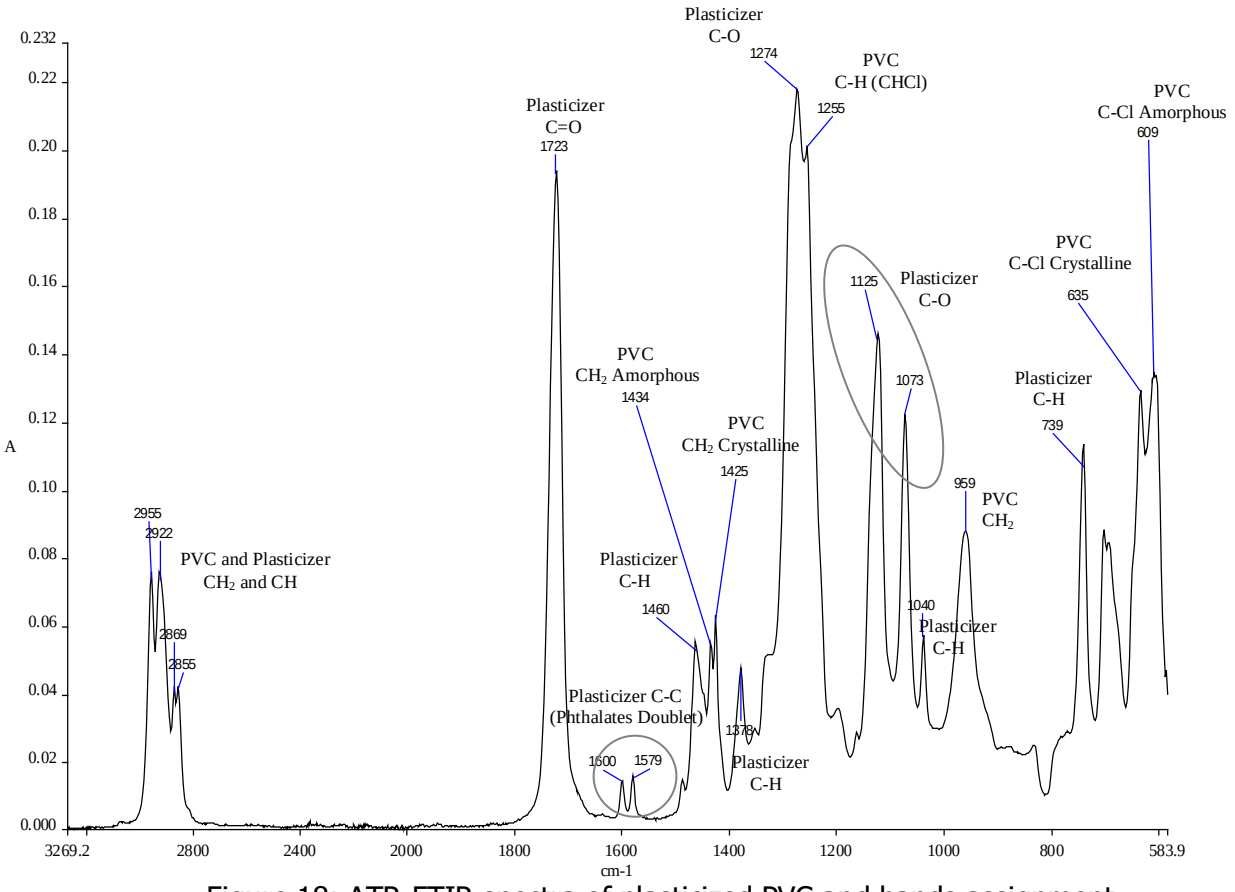


Figure 18: ATR-FTIR spectra of plasticized PVC and bands assignment

The plasticizer in the sample was isolated by Soxhlet extraction during 6 hours with di-isopropyl ether and quantified as 35.5±4% by weight in the material. ATR-FTIR spectroscopic analysis of the extracted plasticizer showed a typical carbonyl peak (C=O) at 1725 cm^{-1} and evidenced the presence of a second compound in the plasticizer from the shoulder at 1732 cm^{-1} in the carbonyl peak (Figure 19).

As it can be seen on the obtained GC-MS chromatogram (Figure 20), adipates and phthalic acid esters were present in the plasticizer, corresponding to a mixture of approximately 96% Di-isononyl phthalate (DINP) (Figure 21-a), as main plasticizer, and 4% dioctyl (2-ethyl hexyl) adipate, (DOA) (Figure 21-b), normally added to improve the temperature properties of the material (Wilkes *et al.*, 2005). This finding, explained the shoulder seen on the plasticizer carbonyl band in the FTIR spectra (Figure 19). While the plasticizer carbonyl peak (C=O) showed a main peak at 1725 cm^{-1} from the di-isononyl phthalate, a shoulder at 1732 cm^{-1} appeared from the minor presence of dioctyl (2-ethyl hexyl) adipate in the mixture.

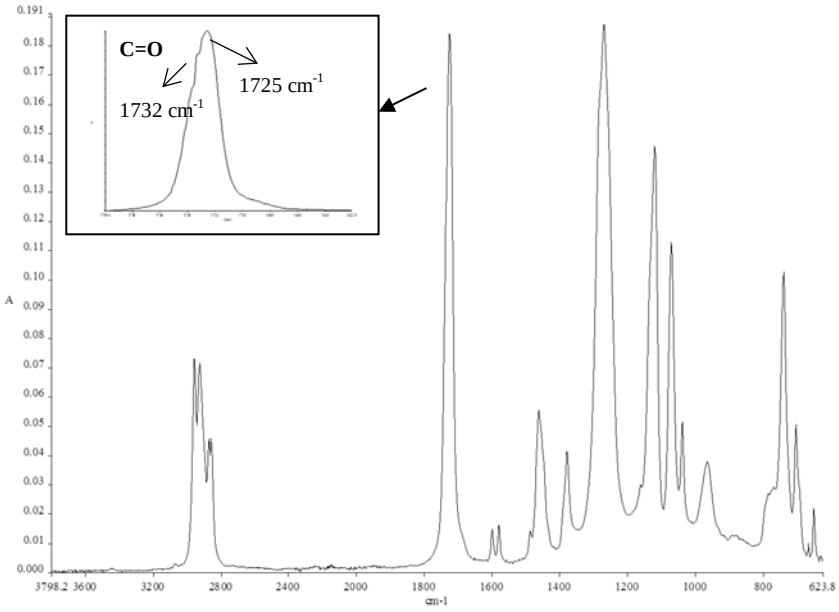


Figure 19: ATR-FTIR spectra of plasticizer extract.

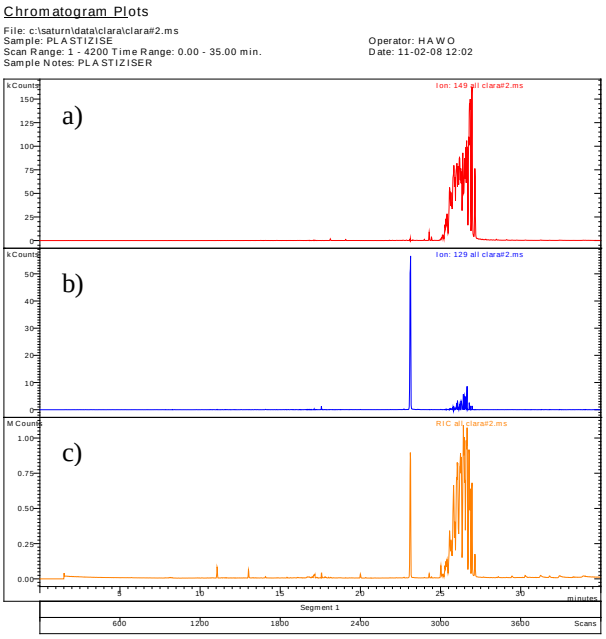
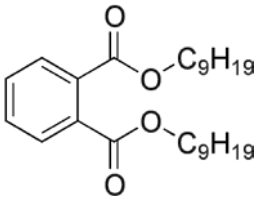


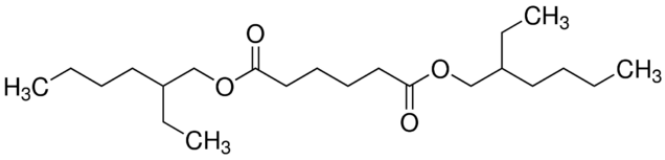
Figure 20: Chromatograms obtained by GC-MS of the plasticizer extracted from the commercial plasticized PVC in the samples using (c) total ion chromatogram (TIC) and single ion monitoring (EIC) at (b) m/z 129 and (a) m/z 149.

Although further additives were not reported on the product data sheet, the ligand of the UV stabilizer 2-(2-hydroxy-5-methylphenyl) benzotriazole (CAS 2440-22-4) (Figure 21-c) was found in the PVC composition by means of GC-MS (Figure 22 and 23).

a)



b)



c)

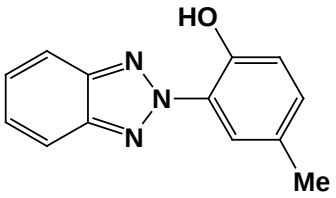


Figure 21. Molecular structures of identified PVC additives: (a) di-isononyl phthalate (DINP) (b) dioctyl (2-ethyl hexyl) adipate (DOA) and (c) UV stabilizer 2-(2-hydroxy-5-methylphenyl)-benzotriazole.

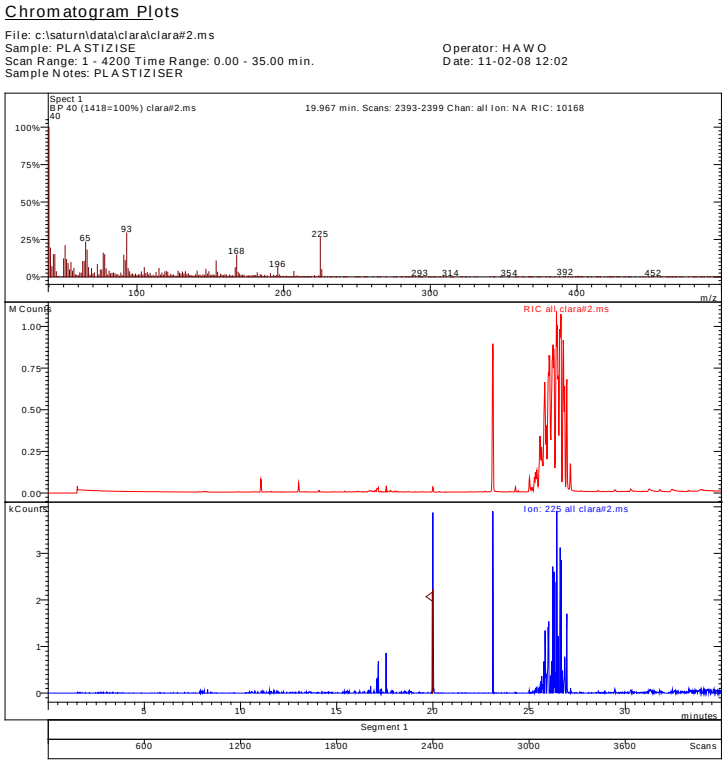


Figure 22: Ion chromatogram and mass spectrum of the "triazol" UV stabilizer in the plasticized PVC sample

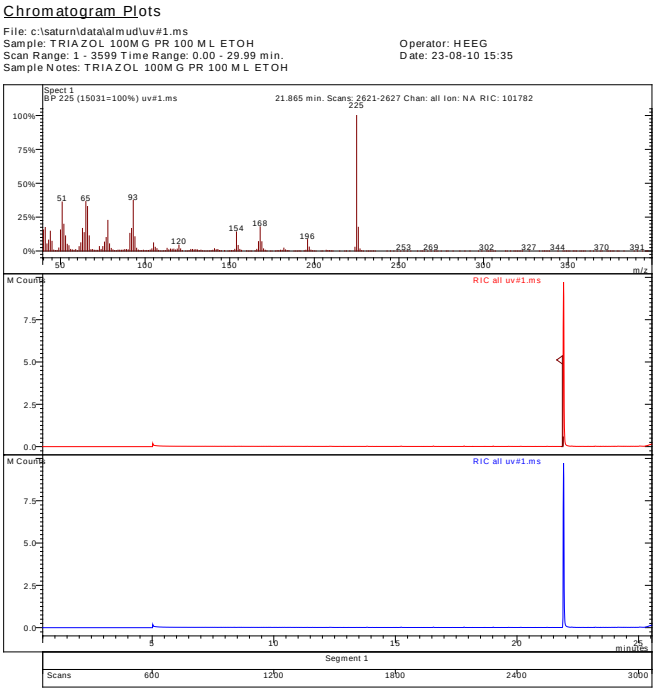


Figure 23: Ion chromatogram of "triazol" UV stabilized in the plasticized PVC sample (middle) and the reference "triazol" (botton).

Elemental analyses by XPS conducted at the National Laboratory for Sustainable Energy (Riso-DTU, Denmark) in some of the samples revealed the presence of Sn and S in moderate concentrations (Figure 24).

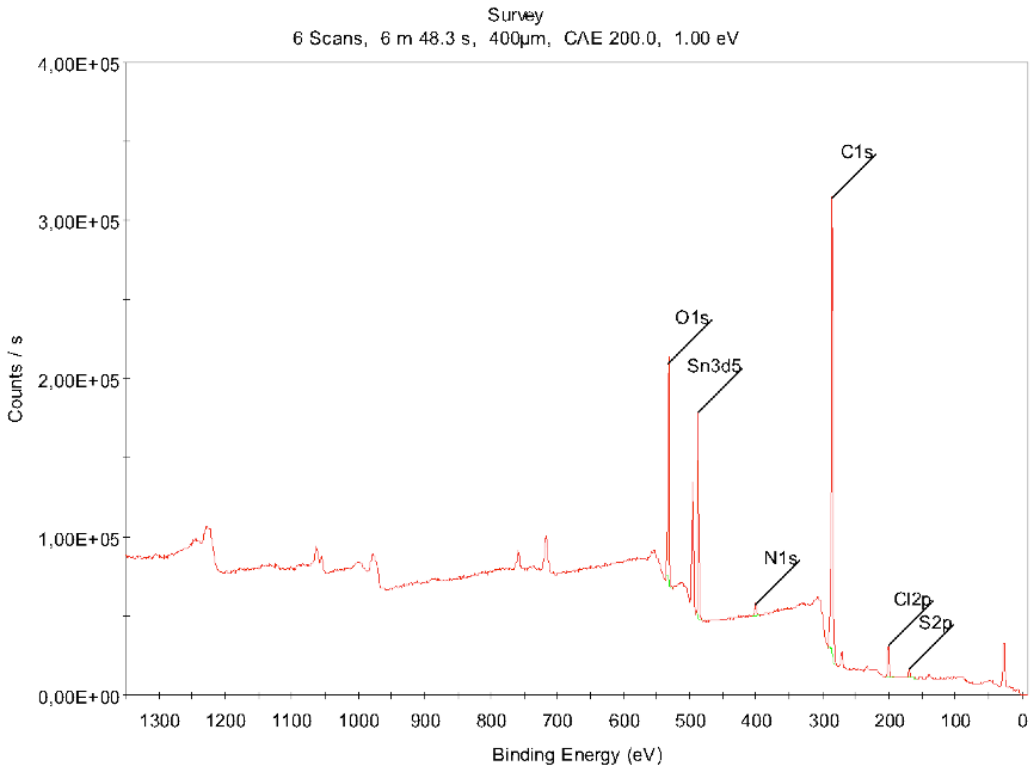
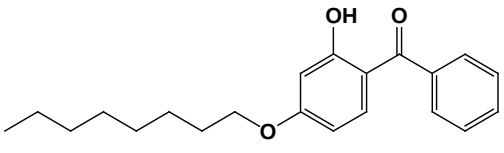


Figure 24: XPS elemental analysis of the commercial plasticized PVC showing the presence of Sn and S on the samples.

Later analyses with XRF and GC-MS also carried out at the National Laboratory for Sustainable Energy (Riso-DTU, Denmark) revealed the presence of the UV stabilizer 2-hydroxy-4-(octyloxy)benzophenone (CAS 1843-05-6) (Figure 25-a) and the ligand of the heat stabilizer 2-ethylhexyl mercaptoacetate (CAS 7659-86-1) (Figure 25-b), which suggested that *organotin* compounds (containing both Sn and S) were added to the commercial PVC as heat stabilizers (Wilkes *et al.* 2005) (Figure 26).

(a)



(b)

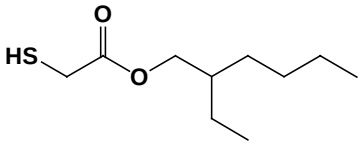


Figure 25. Molecular structures of (a) 2-Hydroxy-4-(octyloxy)benzophenone and (b) mercaptide 2-ethylhexyl mercaptoacetate.

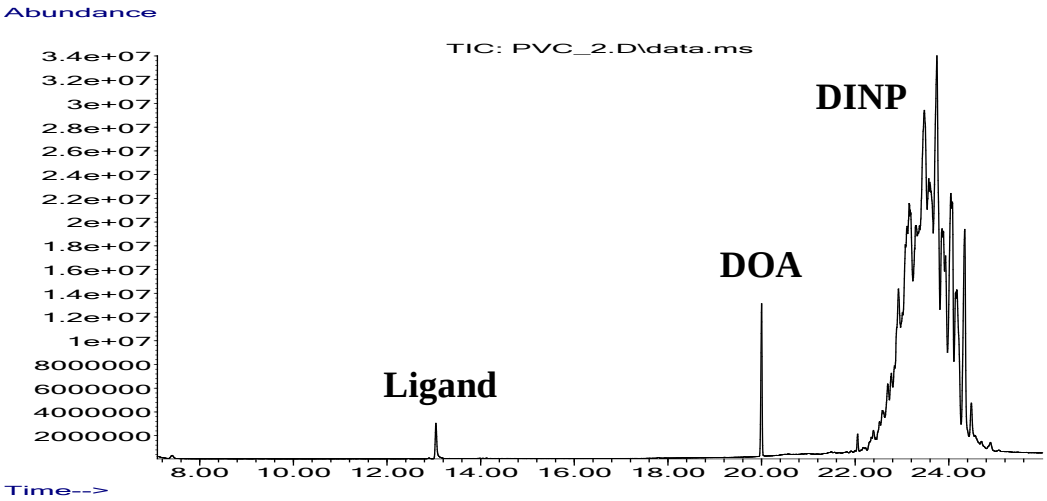


Figure 26. Proportion of plasticizers and the ligand of the ligand of the heat stabilizer 2-ethylhexyl mercaptoacetate in the plasticized PVC.

Regarding the composition of the plasticized PVC doll used in the second part of the research for the testing of cleaning methods on a real plasticized PVC object, several analytical techniques were used (Figure 27).

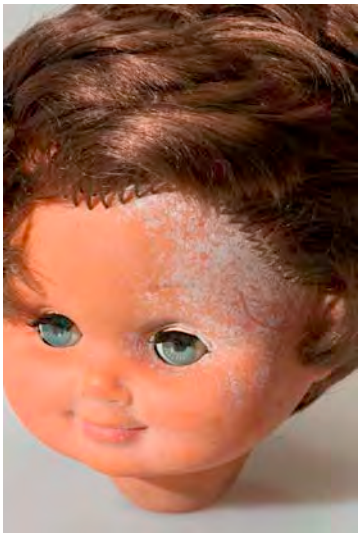


Figure 27. Doll face (detail) with white particles on top

The ATR-FTIR spectrum of the doll perfectly matched with the spectrum of the commercial plasticized PVC used in the first part of the research (Figure 28), indicating that the doll was composed of PVC polymer and a phthalate ester plasticizer.

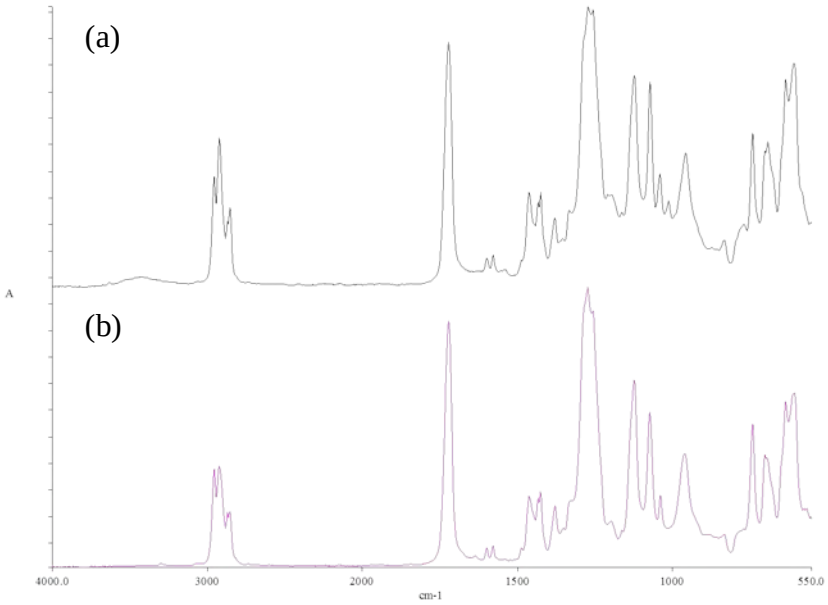


Figure 28. ATR-FTIR spectra of (a) the internal surface of the doll and (b) plasticized PVC reference

In order to identify the phthalate ester plasticizer, it was extracted from the sample, following the same procedure described for commercial plasticized PVC and analyzed by GC-MS. A very dominant signal due to bis (2-ethyl-hexyl) phthalate (DEPH) was identified in the chromatogram, which corresponded to the plasticizer (Figure 29 b and c).

Furthermore, four peaks attributed to the fatty acid 2-ethyl-hexyl esters ($C_{12:0}$, $C_{14:0}$, $C_{16:0}$ $C_{18:0}$), were identified by means of the GC-MS analyses (Figure 29-b). The $C_{12:0}$, $C_{14:0}$, $C_{16:0}$ and $C_{18:0}$ free acids were also detected in amounts corresponding to the $C_{12:0}$ plus $C_{14:0}$ esters.

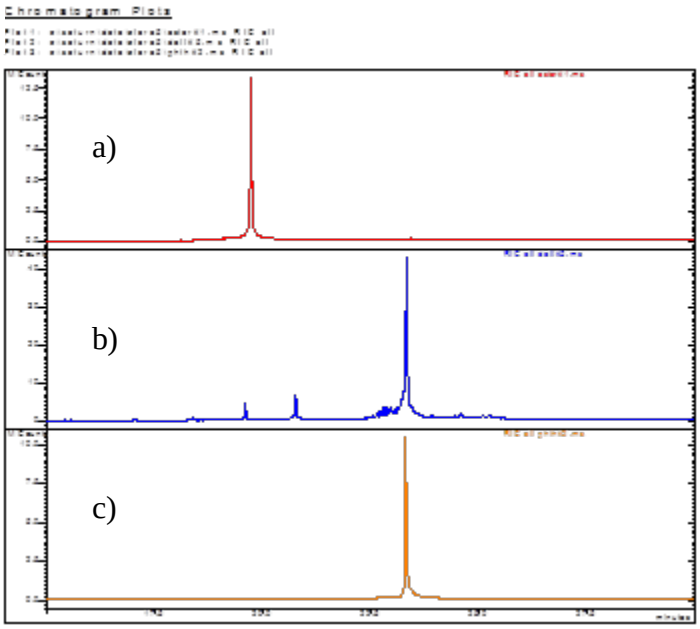


Figure 29. Extracted Ion Chromatogram of (a) 2-ethylhexyl ester of palmitic acid ($C_{16:0}$) (standard reference); (b) doll sample and (c) ethyl-hexyl phthalate (standard reference).

Then, the white particles visible in some areas of the doll surface were mechanically removed an analyzed by ATR-FTIR spectroscopy (Figure 30).

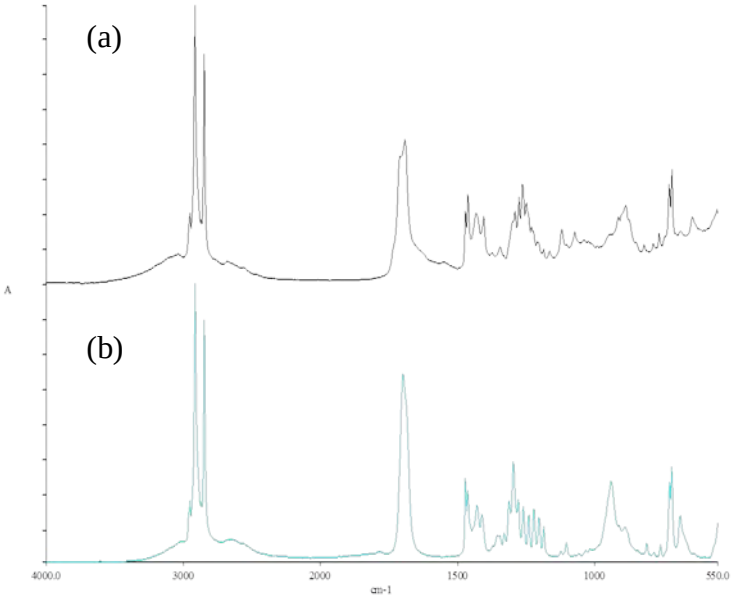


Figure 30. ATR-FTIR spectra of the white particles formed on the doll's surface (a) and stearic acid (b).

Since stearic acid has been reported as a lubricant used in the manufacturing of plasticized PVC objects that can be detached from the polymer and migrate to the surface (Shashoua, 1999), the ATR-FTIR spectrum of the white particles from the doll was compared to the spectrum of a commercial stearic acid used as reference (Merck 97%). The results shown in Figure 30 confirmed this hypothesis, although not a single fatty acid but a mixture of fatty acids was found Figure 31.

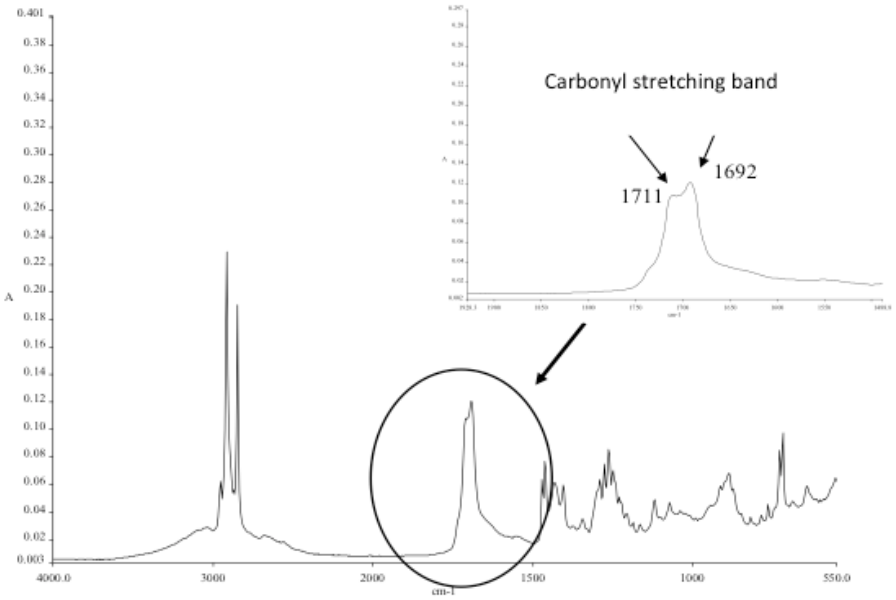


Figure 31. ATR-FTIR spectrum of the white particles formed in the doll surface. The carbonyl band is shown in detail, where the two peaks corresponding to C=O groups.

As shown in Figure 31, in the white powders' spectrum, the band corresponding to C=O stretching absorption was formed by two peaks (Nollet, 2004). These peaks could be assigned to the carbonyl group of two fatty acids, like palmitic and stearic acid (Shereve et al., 1950).

Parallel analyses were run in order to elucidate the composition of the white powders from the doll surface. For this purpose, a sample of the white particles from the doll were immersed for 100 seconds in a 1M aqueous solution of KOH, that was extracted with diisopropyl ether and analysed by GC-MS. The remaining KOH solution was acidified with HCl until pH less that 1 and extracted with diisopropyl ether. The organic phase was analysed by GC-MS. The results confirmed that the white particles were due to a mixture of palmitic (C16:0) and stearic acid (C18:0) accompanied by 2-ethyl-hexyl esters of fatty acid, as was already evidenced by IR spectroscopy (Figure 30).

4.3. Natural and Artificial Ageing

For the investigation of the cleaning in soiled and aged samples, the commercial plasticized PVC was exposed to natural soiling and artificial photo-ageing treatments. For the soiling process, samples of plasticized PVC were left in outdoor conditions for six months avoiding direct rain or sunlight. After the soling process, a mixture of pollutants and soil could be observed on the surface, which made the material suitable for testing the cleaning treatments (see pictures in Figure 32).

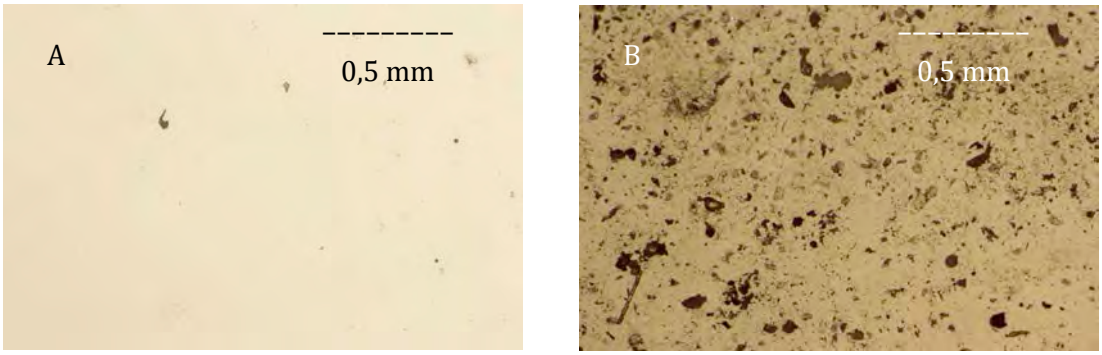


Figure 32: Plasticized PVC samples before (a) and after 6 months of natural soiling in outdoors conditions (b) observed by optical microscopy.

From the SEM images the soil was clearly identified as a diversity of particles, such as dust, fibers and sand (Figure 33).

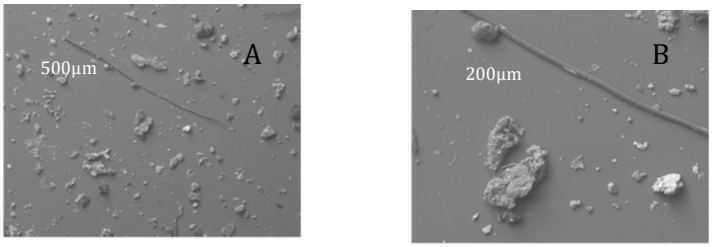


Figure 33: SEM Micrographs of plasticized PVC after soiling (A and B).

PVC polymer absorbs UV radiation below 190-200 nm. Since the UV part of the sunlight radiation starts at 290nm, it is very unlikely that daylight in outdoor conditions causes any degradation to the raw polymer. On the other hand, common

windows glass absorbs over 90% of light below 300nm and the amount of the UV sunlight radiation reaching the surface of plastics objects in indoor environments is reduced. However, many products and defects formed during the processing of the plastic, as well as the plasticizers added to the PVC polymer can absorb UV wavelengths higher than 200 nm. Carbonyl or aromatic groups, for instance, are presented in phthalate ester plasticizers and absorb radiation of wavelengths higher than 290 nm. Furthermore, conjugated double carbon bonds absorb radiation above 250 nm. In these cases, both visible and UV radiations must be considered factors inducing degradation of plasticized PVC.

Based on this approach, photo-ageing conditions were selected to reproduce daylight in the presence of air as main factor of degradation, while temperature was avoided as degradation factor. For this, temperature condition during the artificial photo-again was settled below 60ºC (maximum temperature recommended by the PVC manufacturer: VINK). The illuminance selected was 110000lux, that is the direct normal illuminance or illumination outside in a sunny summer day (average amount of direct normal illuminance in hundred of lux received within a 5.7º field of view centered on the sun (Kalogirou, 2013).

Accelerated ageing was conducted in an ATLAS CI 3000+ Weather-O-Meter. The experiment simulated "outdoor" conditions in order to obtain measureable degradation effects within a reasonable time frame. Lamp and filters selected were those bets reproducing outdoor daylight conditions: a 1,97 kW xenon lamp using Type S borosilicate inner and on outer filters. As shown in (Figure 34), the flexible plasticizer PVC sheet was cut in pieces that fixed in the metallic frames used for ageing in the chamber and exposed to the light only on one side (Figure 35).

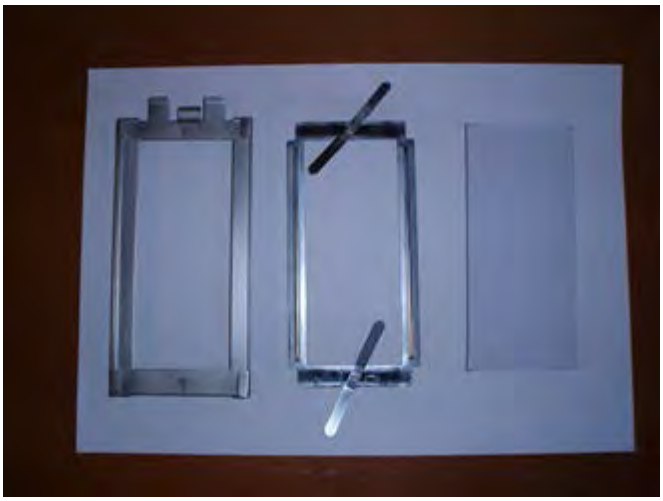


Figure 34: Plasticized PVC cut and metallic frame for ageing

The conditions achieved on the samples were:

- Light level: 110.000 lx
- Accumulated light dose: 73.920.000 lxh
- Temperature in the chamber: 46±1°C
- Black Standard temperature: 61±1°C
- Relative humidity: 54±1%

Figure 35: Plasticized PVC placed within the climatic chamber for ageing.

During the experiment, the irradiance and light levels were 50 $W \cdot m^{-2}$ (at 300-400 nm) and 110.000 lx, respectively. The ageing was carried out until the surface of the samples reached high levels of degradation, which was monitored by retrieving and analyzing the samples at 168 h (1 week), 336 h (2 weeks), 504 h (3 weeks) and 672 h (4 weeks) of exposition (see Figure 36).

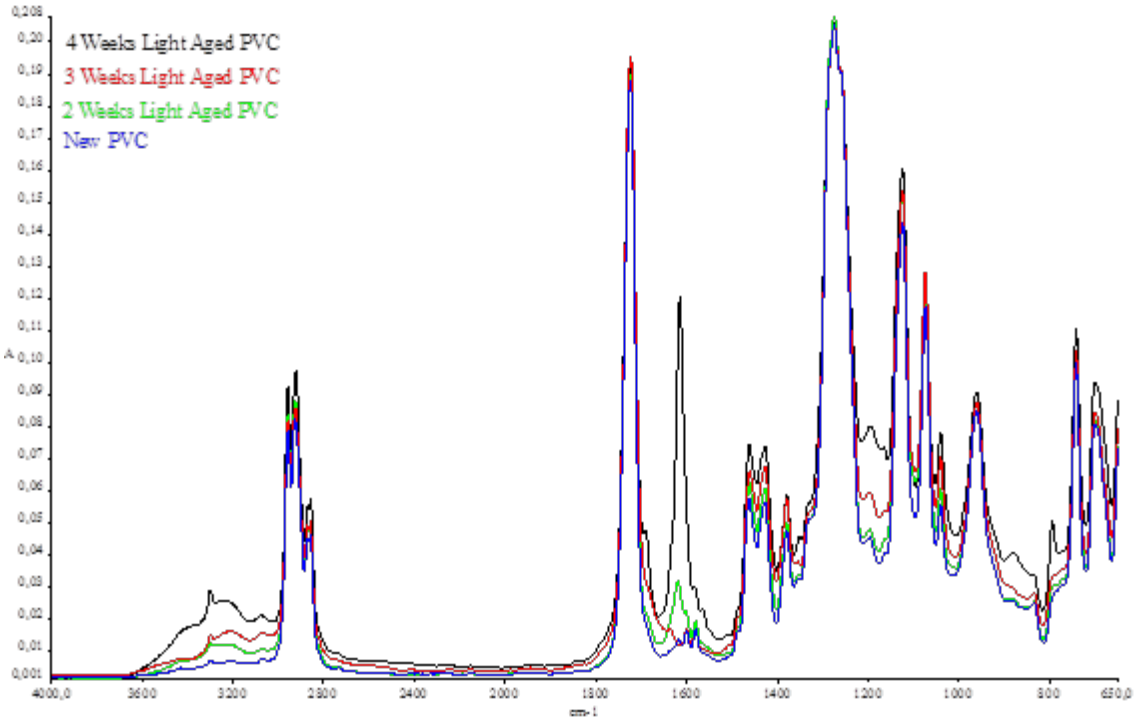


Figure 36: ATR-FTIR spectrum of commercial plasticized PVC before and after 168 h (1 week), 336 h (2 weeks), 504 h (3 weeks) and 672 h (4 weeks) of exposition.

Color and chemical changes were noticed on the samples starting at 336h, but chemical "useful" changes for the cleaning assessment were not achieved until 672 h of exposition, which equaled a dose of 73.920.000 lx·h (672 hours * 110.000 lx), as shown in Figure 37. These changes were detected by the appearance of new peaks in the spectra as a consequence of the formation of degradation products. Their analysis was also part of the research.

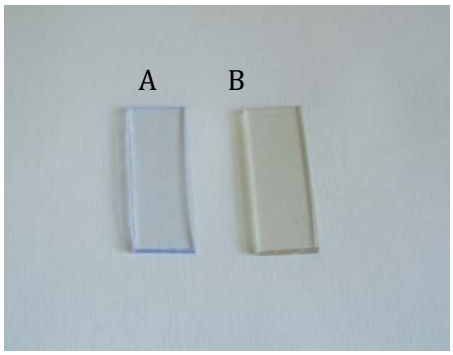


Figure 37: Samples of the commercial plasticized PVC (A) before and (B) after 672h of artificial photo ageing

4.4. Cleaning agents and cleaning performance

The following cleaning agents and procedures were proposed for the cleaning of the plasticized PVC samples in the experimental section (see Figure 38).

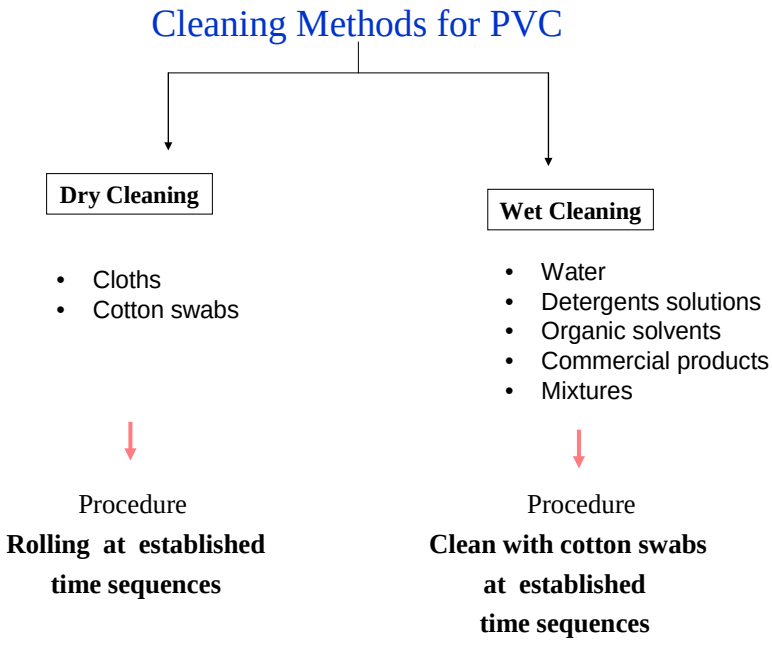


Figure 38: Cleaning methods and procedures

For the dry cleaning, commercialized cloths for plastics artwork cleaning and cotton swabs (Figure 39-a) generally used for cleaning artworks' surfaces were proposed. The commercial cleaners selected were PEI-Cloth™ (Figure 39-b), PEL-Cloth™ Glass (Figure 39-c) and Dust Bunny cloth (Figure 39-d) (supplied by Preservation Equipment Ltd). As can be observed, the texture of the cloths was significantly different. PEI-Cloth™ and PEL-Cloth™ Glass even presented a different weave despite the same chemical composition.

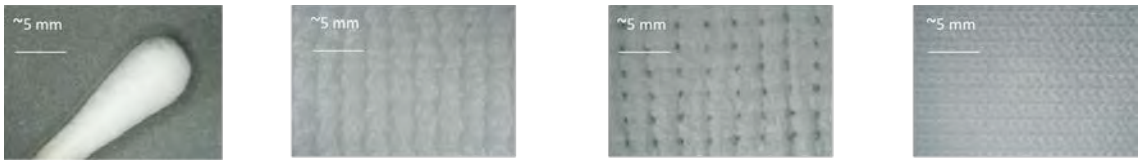


Figure 39: Dry cleaning agents: (a) Cotton Swabs; (b) PEl-Cloth™; (c) PEl-Cloth™ Glass and (d) Dust Bunny cloth.

The cleaning was performed by manually rolling the cloths/cotton swabs onto areas of 1,5-2 cm^2 at fixed time sequences and gentle pressure. The ATR-FTIR analyses demonstrated that PEL-Cloth™ (Figure 40-a) and PEL-Cloth™ Glass (Figure 40-b) spectra corresponded to the superposition of the singles spectra of a polyester (Figure 40-c) and a polyamide (Figure 40-d), certifying that both cloths were composed of a mixture of polyester-polyamide. On the other hand, cotton swabs spectrum (Figure 41-a) matched 100% with a reference spectrum of pure cotton fibers (Figure 41-b), while Dust Bunny cloth spectra (Figure 42-a) was identical to the reference polyamide ATR spectrum (Figure 42-b). Furthermore, the ATR spectra of the commercial dry cleaning agents revealed no type of fibers other than those reported by the supplier. These findings were decisive in the dry cleaning experiments, as the composition of dry cleaning agents was ultimately demonstrated to play a determining role in the results obtained during the cleaning of plasticized PVC.

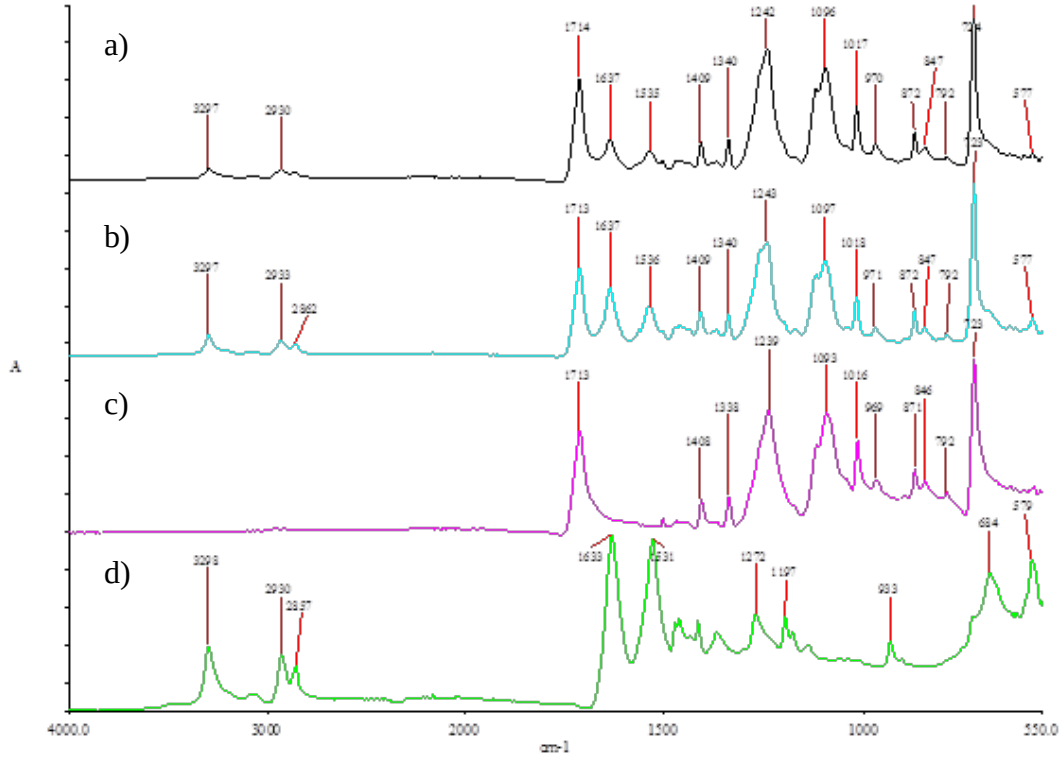


Figure 40: ATR-FTIR spectra: (a) PEL-Cloth™, (b) PEL-Cloth™ Glass, (c) reference of a polyester fabric, (d) reference of a nylon fabric.

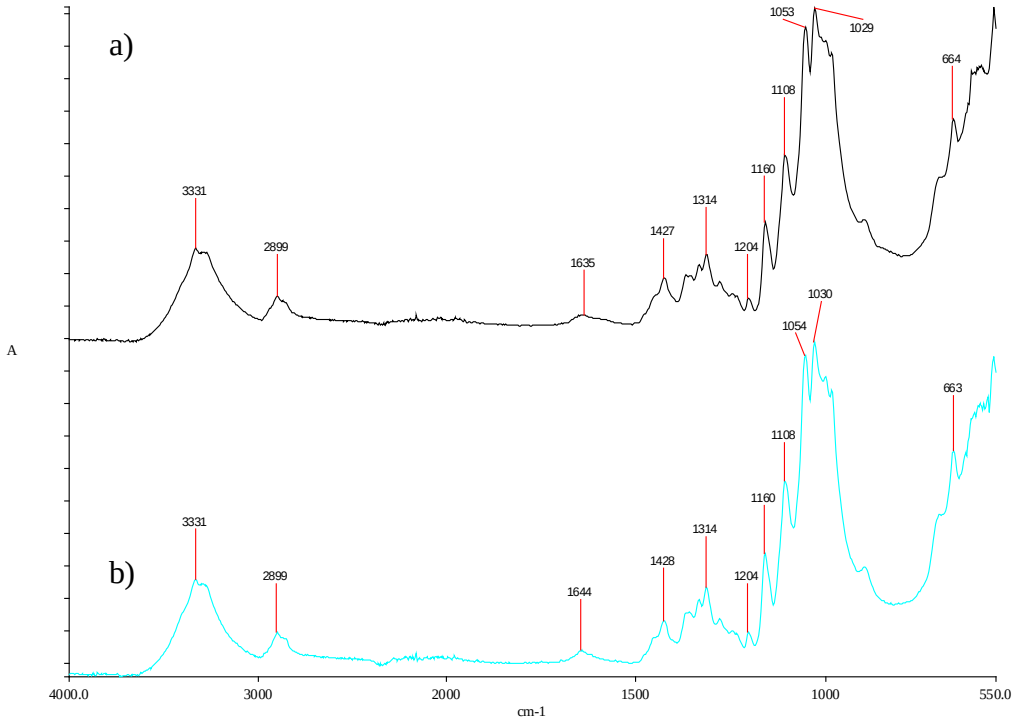


Figure 41: FTIR-ATR spectra of (a) cotton swabs and (b) reference cotton fabric.

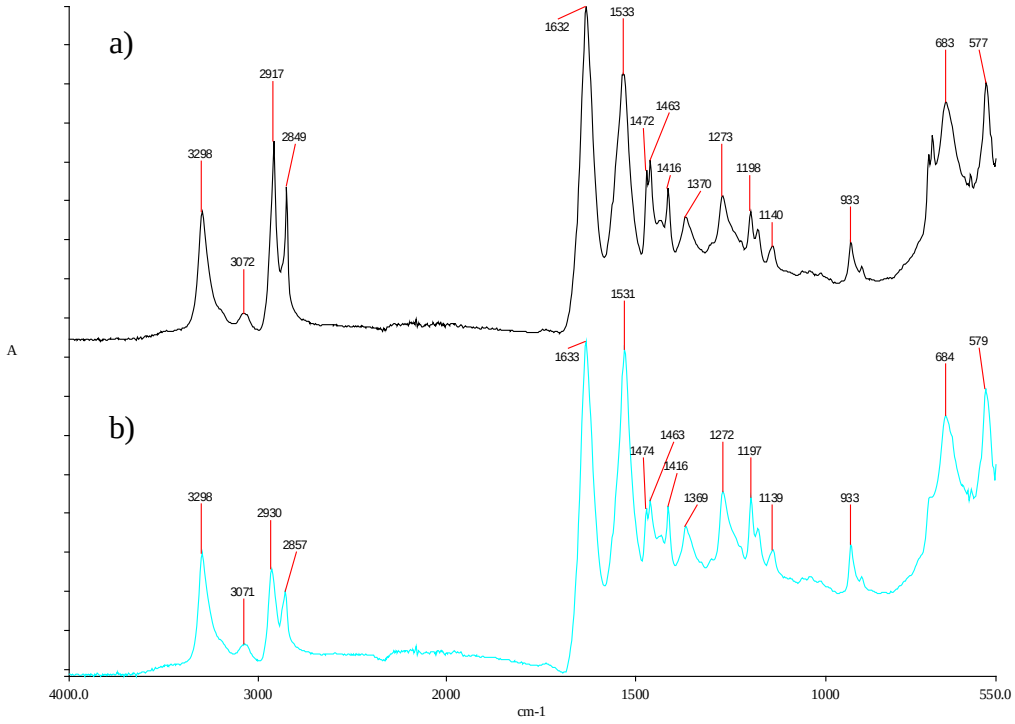


Figure 42: ATR-FTIR spectra of (a) Dust Bunny and (b) reference of a nylon fabric

For the wet cleaning: water, detergent solutions, basic solutions, polar and non-polar organic solvents, aqueous-organic mixtures and commercial cleaners were investigated (Figure 43).

The cleaning of the plasticized PVC samples with the different cleaning solutions was performed by rolling damped cotton swabs onto areas of 1,5-2 cm^2 at fixed time sequences.

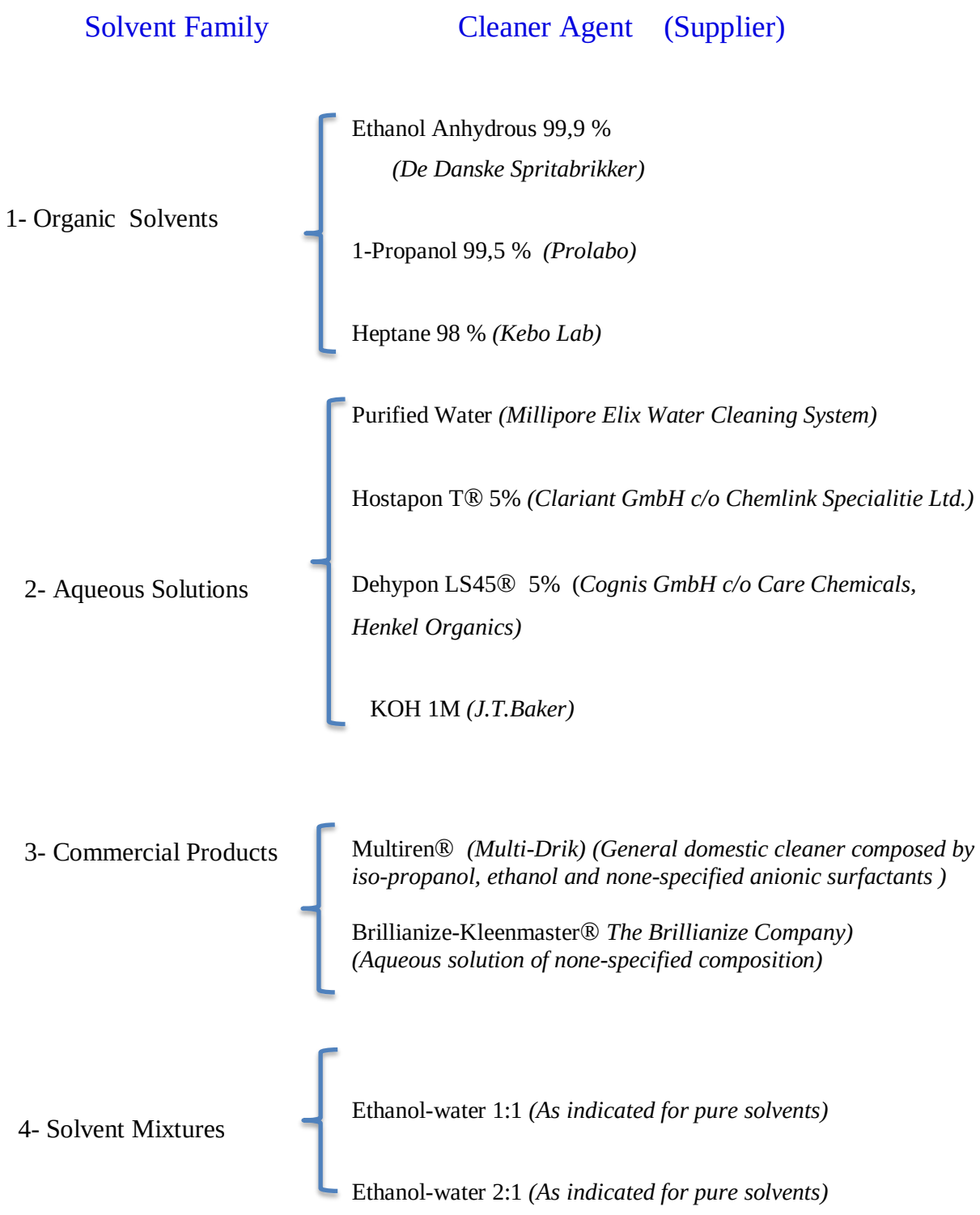


Figure 43: Cleaning agents used in the research.

4.5. Cleaning Examination and Quantification

For the examination of the plasticized PVC surface after the cleaning and the quantification of the cleaning efficiency, the following techniques were applied in this research: eyesight, optical microscopy, spectrocolorimetry, ATR-FTIR spectroscopy and profilometry (Figure 44).

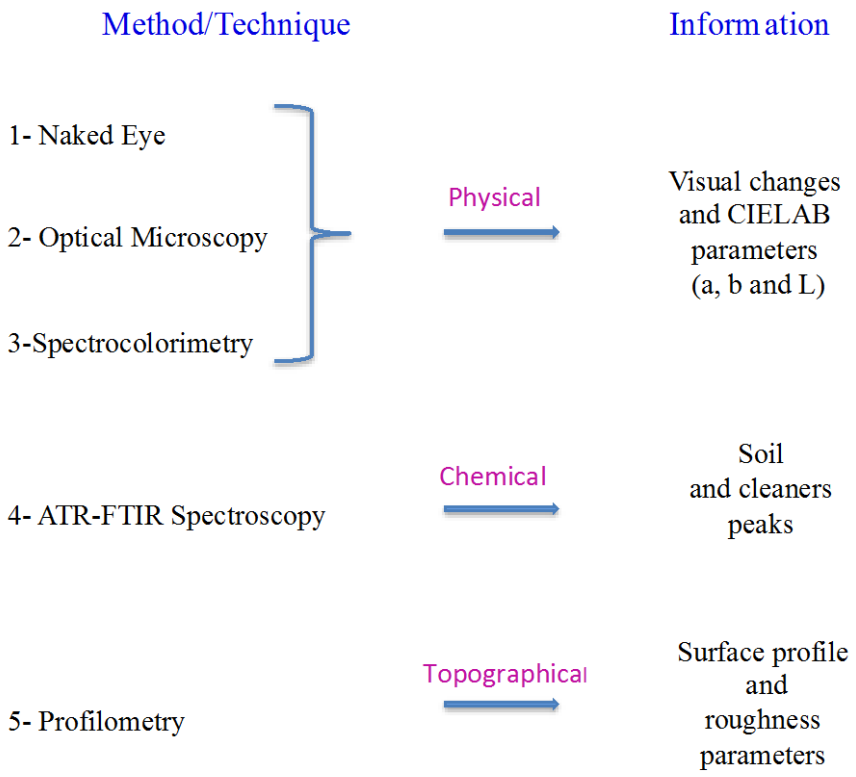


Figure 44: Techniques used for the examination of the plasticized PVC samples' surfaces after the cleaning

Information related to changes in transparency, scratches or colour was gathered by the naked eye and optical microscopy. Micrographs from the sample surface before and after applying the different cleaning methods were taken with an optical microscope at 25x magnification. Visual examination in both macroscopic and microscopic scale was also used as a relative measurement of the cleaning efficiency.

Due to the low penetration of the ATR-FTIR incident beam, (about a few microns), qualitative and quantitative information was collected from the samples surfaces after the cleaning. By qualitative experiments, residues left by the cleaning agents, absorbance of cleaning solutions and morphological alterations of the material caused by the cleanings could be observed. With quantitative analytical techniques, plasticizer extraction and the cleaning efficiency were assessed.

The quantification of the plasticizer extraction during the cleaning was calculated by a relative method, based on the correlation of absorbance (by measuring peak height with respect to the base line) from two main peaks in the plasticized PVC material (Stark and Matuana, 2004): the carbonyl band from the plasticizer at 1722 cm^{-1} and the C-H band from the PVC at 1426 cm^{-1}. To explain this correlation, the "Plasticizer Index (PI)" was proposed as "the percent of plasticizer loss in the sample due to the plasticizer extraction during the cleaning process" and mathematically expressed like:

$$PI\ (\%) = \left(\frac{\left(\frac{Abs_{1722\ cm^{-1}}}{Abs_{1426\ cm^{-1}}}\right)_{after\ cleaning} - \left(\frac{Abs_{1722\ cm^{-1}}}{Abs_{1426\ cm^{-1}}}\right)_{before\ cleaning}}{\left(\frac{Abs_{1722\ cm^{-1}}}{Abs_{1426\ cm^{-1}}}\right)_{before\ cleaning}} \right) \times 100$$

The ATR-FTIR analyses were carried out with the same equipment used for the investigation of the degradation compounds: a Spectrum One Spectrometer (PerkinElmer) with a Diamond/ZnSe crystal and a 458 angle of incidence. During the experiments, all the spectra were recorded in the 4000–550 cm^{-1} range in absorbance mode, and 20 scans. The resolution was set to 4 cm^{-1} for quantitative analysis, while a resolution of 8 cm^{-1} was used for the qualitative analysis. In all the cases, the samples were examined with no preparation and under laboratory conditions. Hence no chemical alterations were produced when measuring, allowing to perform the cleaning under normal conditions usually used in museums and conservation centers.

Spectrocolorimetry was used for the qualitative examination of colour variations during the cleaning by measuring the CIELAB parameters a* (blueness) and b* (yellowness). For this purpose, as soil and degradation particles are darker than the commercial plasticized PVC surface, the increase of the CIELAB parameter L* (lightness) after the cleaning was associated with cleaning efficiency. In order to quantify the cleaning efficiency, the following formula was proposed, where "unsoiled" referred to the original commercial plasticized PVC, while "soiled" referred to the same material after the soiling or photo-ageing process used to produce dirt particles and degradation products on the samples' surface:

$$\text{Cleaning Efficiency } (\%) = \left(\frac{L^*_{cleaned} - L^*_{soiled}}{L^*_{unsoiled} - L^*_{soiled}}\right) \times 100$$

Qualitative information of the surface topography after the cleaning was provided by means of the non-contact profilometer μsurf Explorer and a non-contact profilometer μsurf Mobile (NanoFocus AG, Germany). In both cases: cleaner's residues, scratches, changes on the samples topography and soil removal, were visually identified on the 2D reflection images and 3D images. Since the profile of a soiled surface may change with the removal of the soil by the cleaning, variations of the standard deviation of the height distribution (Sq parameter) were quantified in order to determine the cleaning efficiency. For this purpose, the following equation was used:

$$\text{Cleaning Efficiency } (\%) = \left(\frac{Sq_{cleaned} - Sq_{soiled}}{Sq_{unsoiled} - Sq_{soiled}}\right) \times 100$$

5. DRY CLEANING

Dry cleaning methods have been commonly used for artworks cleaning. However, their use and effects on plastics surfaces have not been deeply investigated. In order to provide a better understanding of dry cleaning methods on plastics surfaces, several dry cleaning agents were proposed and tested on plasticized PVC, which was used as sample material in the current research.

The main purposes targeted were:

a) Examination of the effects caused by dry cleaning methods on plasticized PVC (new and naturally soiled surfaces);

b) Examination of the efficiency of several dry cleaning agents on plasticized PVC (new and naturally soiled surfaces);

c) Investigation of methods for the quantification of the cleaning efficiency on plastics surfaces after dry cleaning treatments. For this, traditional methods based on photocolorimetry were compared against new proposed methods based on topographical measurements;

d) Investigation of the role that the chemical composition and the texture of the dry cleaning agents played during the cleaning of the plasticized PVC surfaces. For this, cloth of different composition and cloth with the same composition but different texture were selected.

Surface modification of plasticized PVC by dry cleaning methods: Consequences for artworks

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Surface modification of plasticized PVC by dry cleaning methods: Consequences for artworks

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ABSTRACT

A study of dry cleaning methods for plasticized PVC has been undertaken using three commercial cloths recommended for plastics artworks, in addition to cotton swabs traditionally used in art conservation. The evaluation of the cleaning has focussed on the efficiency of the cleaners, and the physical and chemical damages caused by the cleaning. The physical and chemical modifications of the PVC surface have been studied by optical microscopy, non-contact profilometry and ATR-FTIR spectroscopy, while spectrocolorimetry and non-contact profilometry have been used for evaluating the cleaning efficiency. The results have shown that the cleaner's composition and the cleaning time play an important role in damaging the plasticized PVC surface. On the contrary, it has not been completely determined if the texture of the cleaning agents' surface had an influence on the cleaning efficiency.

1. Introduction

Plastics are not only part of our daily life but also present as art objects in many collections [1–4]. For years, experts all over the world have studied the problems regarding the conservation of plastics (e.g. [5–7]), but their care and maintenance are still a matter of concern for museums.

Plasticized PVC is a common plastic in both the industry [8] and art collections [2,3] whose cleaning by means of solvents and gels has been proposed and investigated in several studies (e.g. [9,10]). However, based on dry cleaning methods used in conservation (e.g. [11–14]), this research has studied in depth the dry cleaning of plasticized PVC with three commercial clothes recommended for plastics artworks cleaning. In addition, a comparative study has been performed with cotton swabs, which are traditionally used for artworks cleaning but avoided for plastics surfaces cleaning.

As a consequence of mechanical action during cleaning processes, the plasticized PVC surface can be physically and topographically damaged. Detailed information of the roughness and the appearance of the surface after cleaning can be obtained from non-contact techniques as confocal white light profilometry and optical microscopy [12,15,16]. The interaction between the cleaner and the object surface during the cleaning can also produce chemical modifications on the plasticized PVC surface, which can be studied by ATR-FTIR spectroscopy [17,18]. Quantitative and qualitative differences between a dirty surface and a cleaned surface can be observed by colorimetric and profilometric methods, which can be also used for the assessing the cleaning efficiency [19,20].

Besides finding the best dry cleaning method for plasticized PVC, the purpose of this paper was also to provide a methodology of study when dealing with the dry cleaning of a plastic object in general, and hence to help in the preservation of this particular form of cultural heritage.

2. Materials and methods

The plasticized PVC used for this study was provided by the company VINK AS (Denmark), as a colourless flexible sheet of 2 mm thickness (Ref: 109200). The plasticizer was extracted by Soxhlet with di-isopropyl ether for 6 h, and analyzed by GC–MS at Risø-DTU. The percent of plasticizer extracted in the sample was 35.5 ± 0.4% and it was found to be composed of a mixture of diisononyl phthalate (94%, w/w) and dioctyl adipate (6%, w/w). The presence of other additives as lubricants, antioxidants etc., was not reported for the company and was not founded by GC–MS or ATR-FTIR techniques in this study.

The commercial clothes used for the cleaning, were those recommended for plastics artworks: Dust Bunny Cloth, PEL-Cloth™ and PEL-Cloth™ Glass Cloth. These dry cleaners were selected in order to evaluate the role of the chemical composition of the fabrics during the cleaning, and also to compare the effects

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produced by clothes of the same composition but of different weave [21]. The composition shown on the PEL-Cloth™ and PEL-Cloth™ Glass Cloth labels was 70% polyester and 30% polyamide for both products, but no specification was found for Dust Bunny cloth. The cotton swabs composition was indicated as 100% cotton. According to the specifications, none of the cleaner agents contained any solvent or chemicals. Following analyses by ATR-FTIR spectroscopy were made to corroborate the composition of all the cleaners.

The physical and chemical effects of the dry cleaning were studied on unsoiled samples, whereas the cleaning efficiency was tested on naturally soiled samples. The soiling took place from July 08 until January 09 in Copenhagen and the exposition was in outdoor conditions out of direct rain or sunlight.

For a better understanding of the cleaning processes of PVC surfaces in Art Conservation, the cleaning was manually performed by rolling a surface of 1.5 cm^2 with the cleaning agent, at room temperature and mild pressure.

In the case of the unsoiled PVC, three replicate cleanings were performed with each dry cleaner for 10 and 100 s (times selected to evaluate the effect of short and long cleaning periods). In soiled plasticized PVC, also three replicate cleanings were performed with each dry cleaner, but for 30 s, time that was selected as the most suitable standard cleaning time. The temperature on the dry cleaning agent surface was checked during the cleaning processes and no increase was noticed because of the friction. Therefore, chemical variations induced by this factor were ruled out.

The spectra provided by ATR-FTIR spectroscopy, the L^* value (lightness) obtained by spectrocolorimetry and the images acquired from the profilometric studies and optical microscopy were used to evaluate the cleaning effects on the PVC surface. ATR-FTIR spectroscopy and Spectrocolorimetry were used to quantify the cleaning by means of an index of cleaning efficiency [19] calculated from L^* parameters: Cleaning Efficiency Index (%) = (L^*cleaned − L^*soiled)/(L^*unsoiled − L^*soiled) × 100 and from Sq parameters: Cleaning Efficiency Index (%) = (Sq cleaned − Sq soiled)/(Sq unsoiled − Sq soiled) × 100.

Photomicrographs were taken with an optical microscope Axiotech100HD at 25× magnifications. ATR-FTIR analyses were carried out with a Spectrum One Spectrometer (PerkinElmer). The spectra were recorded in absorbance mode, in the 4000–550 cm^{-1} range, at resolution of 4 cm^{-1} and 20 scans, while the surface of the samples was in contact with a Diamond/ZnSe crystal with a 45° angle of incidence. The spectra were analyzed without smoothening the data or baseline correction. The parameter L^* (lightness), of the colour system CIELAB, was measured using a Colorimeter Minolta CM 2600D equipped with Standard Illuminant D65 [22]. The roughness parameter Sq, defined as the standard deviation of the height distribution [23], was calculated for 800 × 800 μm^2 field size surfaces by means of a non-contact profilometer Usurf Explorer, provided by NanoFocus AG [15,24] and equipped with an 800 XS objective. 3D images and reflection images from the surface topography were also provided. Measurements were carried out at a 0.03 μm steps width in the z-direction for unsoiled PVC samples and at a 0.08 μm steps width for soiled PVC samples.

3. Results and discussion

3.1. Physical and chemical evaluation

The Sq values presented in Table 1 show an increase in surface roughness after both 10 s and 100 s cleaning treatments with cottons swabs and Dust Bunny cloth, while the Sq value changed only after 100 s cleaning time, when the cleaning was performed with PEL-Cloth™. In the case of the PEL-Cloth™ Glass Cloth cleaning, there were no significant changes after either 10 s or 100 s cleanings.

Table 1
Sq values and the standard errors of means (±S.E.) measured on unsoiled plasticized PVC, before and after dry cleaning with several cleaners. The step width in the z-direction was 0.03 μm.

Cleaning stage	Sq (μm)	
	t_1 (10 s)	t_2 (100 s)
Before cleaning	0.023 ± 0.006	
After cotton swabs cleaning	0.033 ± 0.003	0.045 ± 0.003
After Dust Bunny cloth cleaning	0.052 ± 0.012	0.064 ± 0.002
After PEL-Cloth™ cleaning	0.027 ± 0.003	0.034 ± 0.001
After PEL-Cloth™ Glass Cloth cleaning	0.027 ± 0.002	0.026 ± 0.002

The roughness profile images provided additional qualitative information about the effects caused by the dry cleaning. The Plasticized PVC surface appeared smooth and homogeneous before any dry cleaning treatment, which was expected from its small Sq value. In correlation with the roughness data (Table 1), the effects caused by the cotton swaps and Dust Bunny cloth were visible even after 10 s cleanings: cotton swabs produced ridges on the plasticized surface and fibres from the Dust Bunny cloth were clearly recognisable after cleaning. On the contrary, no changes were noticed after 10 s cleanings with PEL-Cloth™ and PEL-Cloth™ Glass Cloth, although lightly rough surfaces were visible after 100 s treatments with both cloths.

The plasticized PVC was analyzed by ATR-FTIR spectroscopy [25] (Fig. 1a), as well as the cleaning agents, which resulted in cotton for the cotton swabs, a polyamide for Dust Bunny cloth and a mixture of a polyamide and polyester for both PEL-Cloth™ and PEL-Cloth™ Glass Cloth (Fig. 1c, e, h, j).

No chemical changes in the ATR-FTIR spectrum of plasticized PVC were observed after cleaning for 10 s with cotton swabs, PEL-Cloth™ or PEL-Cloth™ Glass Cloth, but qualitative variations were clearly noticed after 10 s cleanings with Dust Bunny cloth and after 100 s cleanings with all the cleaners (Fig. 1b, d, g, i). In order to understand these alterations, the A_{634}/A_{612} ratio between the C–Cl intensities of the PVC crystalline and amorphous bands [26] was calculated for all the cleanings (Fig. 2a). In addition, the A_{739}/A_{635} ratio between the C–H plasticizer and the C–Cl PVC resin bands [7] was calculated to evaluate if plasticizer was coming to the PVC surface, as a consequence of the cleaning action (Fig. 2b).

The ratio PVC crystalline-PVC amorphous A_{634}/A_{612} (Fig. 2a) significantly decreased after the cleaning with cotton swabs for both 10 s and 100 s, and it slightly decreased when Dust Bunny Cloth and PEL-Cloth™ were used for 100 s cleanings. For the other cleanings, the variation of the ratio laid within the STD error, therefore no modifications could be recognized. On the contrary, the ratio plasticizer–polymer A_{739}/A_{635} increased after cleanings with cotton swabs for 10 s, and after 100 s cleanings in all the cases, which was noteworthy when the cleaning was performed with cotton swabs. This raise of the relation plasticizer/PVC polymer suggested that the plasticizer was being brought from inner to external layers in the surface because of the mechanical action of the cleaning, what could be observed as white spots in the micro pictures (Fig. 3). Other theories that could explain the white spots in the micropictures (Fig. 3), such as migration of any additive in the polymer, were dismissed since no analytical support was founded n the ATR-FTIR spectra (Fig. 1). Besides, no presence of plasticizer on the dry cleaning agents could be identified in the by ATR-FTIR spectroscopy after cleaning.

According to the values of both Fig. 2, the decrease of crystallinity in the PVC polymer after cleaning had a correlation with the increase of plasticizer on the PVC surface. This fact was interpreted as the separation of the PVC chains in the polymer

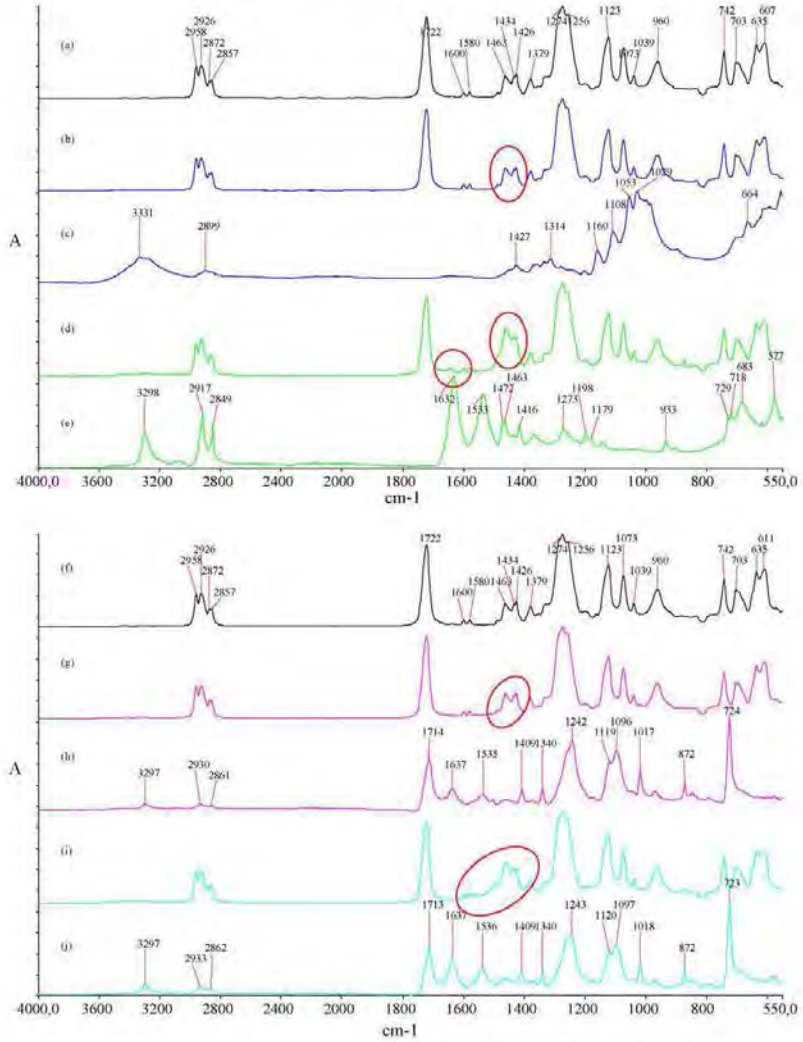

Fig. 1. ATR-FTIR spectra of: plasticized PVC (a), plasticized PVC after cleaning for 100 s with cotton swabs (b), cotton swabs (c), plasticized PVC after cleaning for 100 s with Dust Bunny cloth (d), Dust Bunny cloth (e), plasticized PVC (f), plasticized PVC after cleaning for 100 s with PEL-Cloth™ (g), PEL-Cloth™ (h), plasticized PVC after cleaning for 100 s with PEL-Cloth™ Glass Cloth (i), and PEL-Cloth™ Glass Cloth (j).

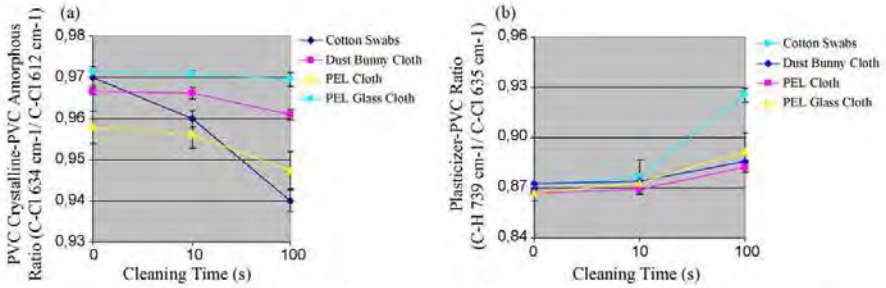

Fig. 2. A_{634}/A_{612} ratio (a) and A_{739}/A_{635} ratio (b) for plasticized PVC before and after dry cleaning. Error bars show the standard error of nine measurements.

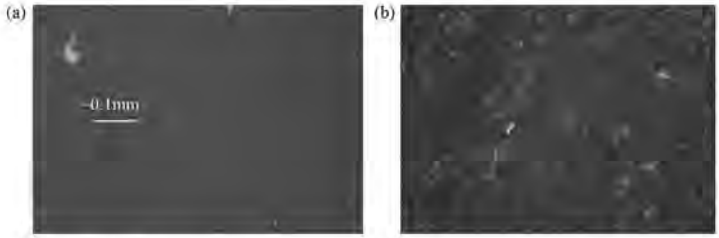

Fig. 3. Example of surface modification after 100 s cleanings, appreciated on micro pictures from plasticized PVC before (a) and after 100 s cleaning with cotton swabs (b).

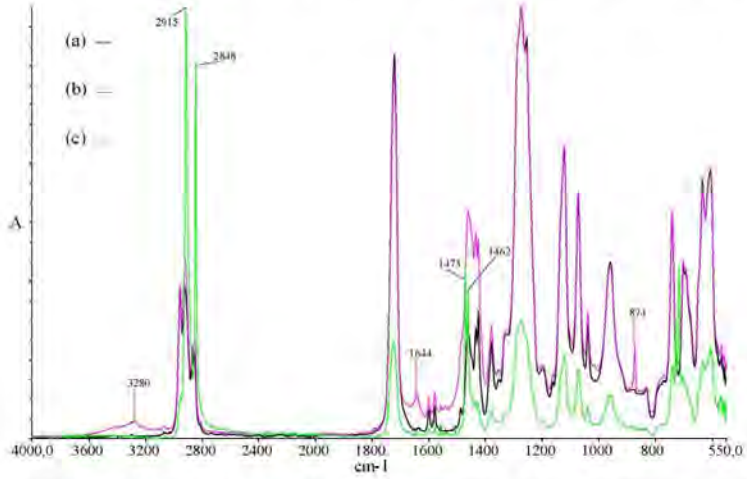

Fig. 4. ATR-FTIR spectra of: plasticized PVC before cleaning (a), plasticized PVC after cleaning with Dust Bunny cloth for 100 s (b), and plasticized PVC with some fibres from Dust Bunny cloth superposed on top (c).

surface because of the plasticizer migration toward the surface, which subsequently decreased the crystallinity of the polymer.

In the particular case of the cleaning with Dust Bunny cloth, new peaks were appreciated in the ATR-FTIR spectrum of plasticized PVC after cleaning with this cleaner (Fig. 4). These peaks were identified [27] with N-groups (3300 and 3080 cm^{-1}) and the Amide I band (1630 cm^{-1}) from polyamides, like the one from the Dust Bunny cloth fibres (Fig. 1c). In addition, it was observed that the newly formed Amide I peak (C=O stretching vibration in the amide group) shifted its position in the spectrum of plasticized PVC (Fig. 4). This fact suggested that some polyamide fibres stayed strongly adhered to the plasticized surface after cleaning, undergoing a modification of the carbonyl bond surroundings [28] due to physical interactions between polar groups in the plasticizer and the nylon fibres. On the contrary, when some fibres of Dust Bunny cloth were superposed on the plasticizer PVC surface, the spectrum was clearly different to the one recorded after the dry cleaning, what supported the previous supposition (Fig. 4). In addition, a parallel cleaning test with Dust Bunny cloth performed on non-plasticized PVC (VINK Ref-105222), showed no variations in its ATR-FTIR spectrum and only some scratches on the surface after cleaning, what pointed the role of the plasticized in the interaction PVC-cloth's fibres during the cleaning.

3.2. Evaluation of the cleaning efficiency

3.2.1. Spectrocolorimetry

Since the plasticized PVC surface became darker after natural outdoor soiling (mixture of dust, sand and fibres), the rise in L^* value (lightness) after cleaning was identified with soil removal. However, even though the L^* value increased after all the cleanings, (Table 2), the efficiency of the cleaners was remarkably different as shown by the Cleaning Efficiency Index by Spectrocolorimetry (Fig. 5a). PEL-Cloth™ seemed to be the most efficient cleaner

Table 2
L^* values and the standard errors of means (±S.E.) of unsoiled and soiled plasticized PVC, before and after dry cleaning with several cleaners.

Cleaning stage	L^* value (D65)
Before soiling	90.9 ± 0.0
After soiling	85.2 ± 0.1
After cotton swabs cleaning	85.9 ± 0.3
After Dust Bunny cloth cleaning	88.3 ± 0.1
After PEL-Cloth™ cleaning	89.6 ± 0.0
After PEL-Cloth™ Glass Cloth cleaning	88.4 ± 0.1

Table 3
Sq values and the standard errors of means (±S.E.) measured on unsoiled and soiled plasticized PVC, before and after dry cleaning with several cleaners. The step width in the z-direction was 0.08 μm.

Cleaning stage	Sq (μm)
Before Soiling	0.04 ± 0.00
After Soiling	2.32 ± 0.18
After cotton swabs cleaning	0.27 ± 0.05
After Dust Bunny cloth cleaning	0.12 ± 0.01
After PEL-Cloth™ cleaning	0.16 ± 0.02
After PEL-Cloth™ Glass Cloth cleaning	0.16 ± 0.01

safest dry cleaning agents for plasticized PVC, as long as they were used for short-term cleanings.

In addition, the experiments proved that cloths of the same chemical composition produced similar chemical and physical alterations, whereas cloths of different composition produced no comparable chemical or physical effects, concluding that the plasticized PVC was clearly sensitive to the chemical features of the cleaning agent.

Regarding the effectiveness, both the Cleaning Efficiency Index by colorimetric measurements and reflection images showed the cleanest surface after PEL-Cloth™ cleaning; however the Cleaning Efficiency Index values calculated by profilometry were not in clear agreement, and hence the relation between the cleaning efficiency and the cleaning agent texture remained uncertain after this study.

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6. WET CLEANING

Wet cleaning methods have been commonly used for artworks cleaning. However, their use and effects on plastics surfaces have not been deeply investigated. In order to provide a better understanding of wet cleaning methods on plastics surfaces, several cleaning solutions were proposed and tested on plasticized PVC, which was used as sample material in the current research.

The main purposes targeted were:

a) Examination of the effects caused by wet cleaning methods on plasticized PVC surfaces (new and artificially degraded surfaces);

b) Examination of the efficiency of several cleaning solutions on plasticized PVC (new and artificially degraded surfaces);

c) Investigation of the role that the chemical composition of the cleaning solutions played during the cleaning of the plasticized PVC surfaces. For this, a specific selection of cleaning solutions of different chemical composition were tested;

d) Comparison of commercial cleaners against lab-made cleaning solutions for the cleaning of plasticized PVC

e) Evaluation of cleaning methods proposed in conservation for the cleaning of plasticized PVC artworks,

f) Finding organic mixtures suitable for the cleaning of plasticized PVC;

g) Investigation of methods for the quantification of the cleaning efficiency on plastics surfaces after wet cleaning treatments. For this, traditional methods based on photocolorimetry were compared against new proposed methods based on topographical measurements;

h) Quantitative examination of the damages produced by cleaning solutions on plasticized PVC surfaces by means of a reproducible mathematical approach.

A model approach for finding cleaning solutions for plasticized poly(vinyl chloride) surfaces of collections objects

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A MODEL APPROACH FOR FINDING CLEANING SOLUTIONS FOR PLASTICIZED POLY(VINYL CHLORIDE) SURFACES OF COLLECTIONS OBJECTS

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This study focused on developing a surface cleaning treatment for one type of commercially available plasticized poly(vinyl chloride). The effects of cleaning solutions on samples of plasticized poly(vinyl chloride) were examined by several methods. The sample surface, prior to and after artificial photo-aging, was cleaned with several selected cleaning agents and examined physically (visual examination and under magnification) and chemically (attenuated total reflectance-Fourier transform infrared spectroscopy and gas chromatography-mass spectrometry). More than one type of effective cleaning solutions for the plasticized poly(vinyl chloride) used in the study was found. In addition, a specific method to tailor cleaning mixtures for plasticized poly(vinyl chloride) objects was developed by means of Hildebrand solubility parameters and the formulation of a Plasticizer Index calculated by quantitative measurements of the plasticizer obtained by attenuated total reflection Fourier transform infrared spectroscopy. Since this type of plastic material posed a standard cleaning challenge, the treatment described in this study can serve as a model or guideline for the investigation of additional cleaning methods for plasticized poly(vinyl chloride) objects.

KEYWORDS: *ATR-FTIR spectroscopy, plasticized PVC, cleaning plastic works of art*

1. INTRODUCTION

Plastics are complex materials that present an enormous diversity of chemical structures (Mills and White 1994). Several studies have already addressed the degradation and conservation of plastics (e.g., Blank 1990; Quye and Williamson 1999; van Oosten *et al.* 2002), but only a few have provided guidelines for their cleaning (e.g., Budden 1991; Morgan 1991; Shashoua 2008). It is unlikely that an ideal surface cleaning treatment exists for all situations, because of the wide variety of plastic materials, formulation, degradation mechanisms, type of soiling, and even the shape of the object. Instead, it is likely that individualized treatments will still need to be developed and evaluated, as is commonly done for other collection materials such as paints.

Surface cleaning is usually a treatment to reduce soiling. In general, soiling is a combination of different substances and particles, such as fatty acids and triglycerides from human-based sebum (Tikka *et al.* 2004), natural oils, sand, insect fragments, fibers, and skin (Hun Yoon and Brimblecombe 2001). Other types of compounds may also be encountered on the artwork surface, such as degraded adhesives and remains of previous restorations (Huys and van Oosten 2005), sticky tape and labels from storage, or degradation products formed during the natural aging of the object. The deposit of dust, degradation products, pollutants, etc., on the surface of a work of art may aggravate the degradation processes, creating a risk to the effective conservation of the material and making the removal of such products from the surface mandatory. In addition, dust and pollutants accumulated on the surface of a work of art may adversely affect the appearance, leading the viewer to focus attention on the obscuring soil rather than on the work itself. Therefore, a robust cleaning process is usually essential for the preservation of both the visual appreciation and material aspects of a work of art.

Plastics formulated with plasticizers and stabilizers present particular cleaning challenges, for some of the deposits that accrete on the surface and attract

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particulate soiling are also often integral components in the solid material. In general, plasticizers are additives that attach non-covalently to the polymer chains and confer plasticity to the material. Thus, reducing the concentration of this additive makes the polymer harder and less resistant to impacts. In the case of thin plasticized sheets, loss of plasticizer has major effects and may lead to stiffness and cracking of the material. Cleaning surface deposits of exuded plasticizer risks leaching additional and essential plasiticizer or other additives from the bulk, which might compromise its physical properties, appearance, or stability (Sale 1988), or encourage exudation of additional material to the surface. Residues left on the surface after cleaning may adversely affect the perception of the surface by loss of gloss and color modifications (Blank 1990). In addition, the chemical alteration of the surface due to absorption of solvents may produce a swelling of the surface, as well as yellowing or darkening due to photochemical reactions (Rabek 1996).

This challenge of surface cleaning of plastics and the decision whether to undertake such surface cleaning are similarly faced in the cleaning of other materials, such as oil and acrylic paints. As in those other treatments, however, the decision to treat is not a purely technical one. From both the conservation and historic point of view, original materials belonging to the work of art should be preserved if they are not a danger to the preservation of the material or interfere with the aesthetic aspect of the piece, since they are inherent to the work, as well as being considered as of historical interest, providing information about the artistic process or the object's history. Thus, the plasticizer inside a polymer is both an original component of the material and a key contributor to its physical properties. However, when the plasticizer has migrated from the bulk to the surface of the material, the surface becomes sticky, and that enhances the attachment of pollutants and dirt to the surface, causing conservation and aesthetic problems. In this case, the plasticizer should be removed from the plastic surface by means that avoid the removal of plasticizer from the bulk.

This paper describes the development of a cleaning treatment for a common surface soiling problem in many plastics, the accretion of plasticizer and associated degradation products. This study focuses on a particular plastic, a plasticized poly(vinyl chloride) (PVC), which is one of the most common plastics found in museum and private art collections (Shashoua 2001). In addition to being very commonly encountered as part of artifacts, plasticized PVC has been identified as a material that suffers from degradation in museum collections (Shashoua 2001, 2003). The degradation layer formed during the aging of the material may protect the underlying surface from further degradation (Rabek 1995), but it may also increase the yellowing and darkening of the material and enhance its degradation by the attachment of particles and pollutants to the sticky degraded surface. Therefore, in order to evaluate the effectiveness of cleaning methods on degraded plasticized PVC material, several cleaning solutions were tested on artificially aged samples. It is was mentioned above that controversial issues arise from the decision whether degradation products must be preserved or eliminated from a work of art, and these choices must be assessed in each particular case. However, this important ethical concern was outside of the scope this paper, and consequently it will not be discussed further here.

Commercial plasticized PVC was used as test material in this research project. While this choice limited the information available about the exact composition of the material, it was decided that it was only important that the selected plastic reasonably represent a material on a collection object and demonstrate a condition that would impact a surface cleaning treatment. Because of this selection of a single commercial product, the developed treatment cannot be proposed as a universal one. But the methods by which the treatment options have been explored here and the criteria for the final selections may be useful in future efforts to identify tailored surface cleaning treatments. In this work, a model of the surface interactions is described which may also serve as a guide in the consideration of candidate cleaning agents.

Using a framework developed in previous research, which focused on the effects caused by dry-cleaning methods on a commercial plasticized PVC (Morales Muñoz 2010), the current investigation studied the cleaning of this same material with wet cleaning methods. For this purpose, and based on the description of the different types of soiling mentioned above, a selection of cleaning solutions was chosen to cover the cleaning of the wide range of substances usually removed from the surface of works of art, but specifically applicable to plasticized PVC materials. These candidate cleaning agents included water, detergent solutions, alkaline solutions, polar and non-polar organic solvents, aqueous-organic mixtures, and commercial cleaners (table 1). The cleaning agents were evaluated not for their ability to remove surface soiling, which would vary with specific soiling components, but for their effectiveness in removing common surface deposits, mainly plasticizers and degradation products, while leaving little residue. The penetration of the cleaning agents into the plastic was also measured, because of its importance in the extraction of material (mainly plasticizers or additives) from the bulk plastic, which can alter its physical properties, appearance, or stability. The more appropriate cleaning agents would be those which removed surface deposits, leave no residues, and do not penetrate below the surface. Those

TABLE 1. CLEANING AGENTS USED AND DESCRIPTION OF THE CLEANING PROCEDURES APPLIED

	Cleaning agent *(Supplier)*	Cleaning procedure
Organic solvents	Ethanol, anhydrous, 99.9% (De Danske Spritfabrikker) 1-Propanol, 99.5% (Prolabo) Heptane 98% (Kebo Lab)	Applied on the surface by wiping with cotton swabs in sequences of 5 seconds (until 100 seconds) and air
Aqueous solutions	Deionized water (Millipore Elix Water Cleaning System) Hostapon T 5% aqueous (Clariant GmbH c/o Chemlink Specialities Ltd.) Dehypon LS45 5% aqueous (Cognis GmbH c/o Care Chemicals, Henkel Organics) KOH 1M aqueous (J.T. Baker)	Applied on the surface by wiping with cotton swabs in sequences of 5 seconds (until 100 seconds) Rinsed with cotton swabs damp in DI water and air-dried (2 sequences of 5 seconds)
Commercial products	Multiren (Multi-Drik) Brillianize-Kleenmaster (The Brillianize Company)	Multiren was applied on the surface in sequences of 5 seconds (until 100 seconds) and dried by wiping with cotton swabs Brillianize was applied following the product's instructions: apply onto the surface and remove with clean cotton swabs
Mixtures	Ethanol–water 2 : 1 v:v Ethanol–water 1 : 1 v:v (As indicated for pure solvents)	Applied on the surface by wiping with cotton swabs in sequences of 5 seconds (until 100 seconds) and dried

cleaning solutions that were found safe and effective for undegraded plasticized PVC samples were tested on artificially aged samples in order to test their effect on degraded plasticized PVC.

2. EXPERIMENTAL

2.1 SAMPLE MATERIALS

Colorless plasticized PVC sheets of 2 mm thickness (from the Danish distributor of the company Vink) were used as test material (Product reference: 109200). The product was manufactured by Extruflex, a company that specializes in extruded PVC products sold as flexible sheets, which may be used as heavy curtains, e.g., for use in industrial workshops. The selection of this plastic was primarily due to its extremely flat surface, which made sensitive optical examination and spectroscopic measurement possible. The flat sample surface (shown in fig. 1a) was particularly essential for the attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy (Cooke *et al.* 1999) as described in the Appendix. The evenness and uniformity of the plastic material also aided assessments of color or gloss, which were performed in a prior investigation (Morales Muñoz 2010), and helped to homogeneously age the plasticized PVC samples surfaces. In addition, the plasticized PVC sheet could easily be cut into smaller pieces, which helped in the undertaking of some of the analyses.

Detailed data sheets describing various physical properties of this commercial PVC product were supplied by the companies, but no information was given regarding the specific composition of the plasticizers or heat and UV stabilizers used. Thus, further analyses with gas chromatography-mass spectrometry (GC-MS), x-ray fluorescence (XRF) spectroscopy, and x-ray photoelectron spectroscopy (XPS), described in the Appendix, were done to identify these compounds. In an earlier publication (Morales Muñoz 2010) the plasticizer content of this PVC material was analysed by gravimetry to be approximately 35% by weight. In this study, those plasticizer compounds were identified by GC-MS as a mixture of 96% dinonyl phthalate, a common major plasticizer (Hutzinge and Staples 2003), and 4% di-2-ethylhexyl adipate (DOA), which is an aliphatic diester commonly used to improve the low temperature properties of the material (Wilkes

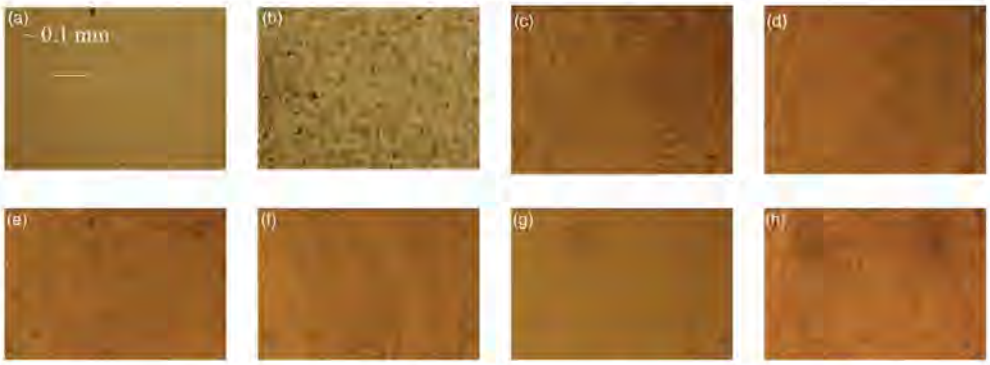

FIG. 1. Photomicrographs (25×magnification) of the plasticized poly(vinyl chloride) (PVC) surface. Film surface before aging (a), after artificial aging (b), and after artificial aging and 10 seconds cleaning with: deionized water (c), ethanol–deionized water 1 : 1 v:v (d), 1 M aqueous KOH (e), Multiren (f), 5% aqueous Hostapon T (g), and Brillianize-Kleenmaster (h).

et al. 2005). In addition, GC-MS revealed the UV stabilizer 2-(2-hydroxy-5-methylphenyl) benzotriazole (CAS 2440-22-4) in the PVC composition. Even though XPS could not be recommended as a routine analytical method for plasticized PVC due to the relatively high vapor pressure of the plasticizers, tin and sulfur were detected by means of this technique, which suggested the presence of organotin mercaptide compounds (composed of Sn and S), commonly used as heat stabilizers in PVC (Wilkes *et al.* 2005). A subsequent batch of the PVC investigated by XRF and GC-MS at the National Laboratory for Sustainable Energy (Riso-DTU, Denmark) was found to contain Sn (0.17%) and S (0.15%). The presence of the mercaptide 2-ethylhexyl mercaptoacetate (CAS 7659-86-1) could also be confirmed. The UV and heat stabilizers were present in very small concentrations, compared to the plasticizers in this PVC.

To simulate the degraded plastic encountered on aged collection objects, the commercial PVC material used in this investigation was artificially aged in a xenon-arc weathering chamber until a degradation layer was visible on the surface. As a consequence of the artificial aging process, the plasticized PVC surface became visibly darker and more yellow. An external layer corresponding to degradation products was also noticeable on the PVC surface through the optical microscope (fig. 1b). In order to understand the nature of these products, samples of the degradation layer were mechanically removed and analyzed by means of ATR-FTIR spectrometry and GC-MS. The presence of several degradation products (Williams and Gerrard 1983; Genova-Dimitrova 1991) were detected in the plasticized PVC ATR-FTIR spectrum (fig. 2): alcohols (O–H vibration at 3300–3200 cm^{-1}), carboxylic acid compounds (O–H and C=O vibrations at 3300–3200 and 1685 cm^{-1}, respectively), alkenes (C=C absorption at 1616 cm^{-1}), aromatic derivatives (band at 1562 cm^{-1}), as well as a significant quantity of plasticizer migrated to the surface during the photo-aging process. Furthermore C_9-alcohols, semi-esters, benzoates, and phthalic anhydride were identified by GC-MS (fig. 3).

2.2 CLEANING AGENT SELECTION

Following other investigations of plasticized PVC cleaning (Fairbrass 1999; Shashoua 2008), deionized water was included as the first cleaning agent. Organic solvents, which are often used in conservation practice, have been discouraged for use in cleaning plasticized PVC (Sale 1993; Shashoua 2001). However, organic solvents such as ethanol and Shellsol A100 have been reported to remove specific compounds like adhesives or labels from plasticized PVC plastic surfaces (Huys and van Oosten 2005). Therefore, organic solvents were included in this investigation in order to re-examine their suitability for cleaning plasticized PVC. The organic solvents used for the cleaning were selected after carefully considering both the PVC and plasticizer properties and the Hildebrand Parameter (the numerical value that indicates the relative solvency behavior of a solvent). According to the chemical properties, pure PVC is a polymer resistant to hydrolysis reactions (Wiles 1993). The datasheet provided by the manufacturer claims the material to be unaffected by alcohols, non-polar solvents, and strong bases. On the other hand, the Hildebrand solubility parameter establishes that two compounds are soluble only when their solubility parameters are close to each other. Therefore, organic solvents with different solvent parameters from water (table 2), such as ethanol, propanol, and heptane, as well as mixtures of ethanol with water, may be suitable for the cleaning.

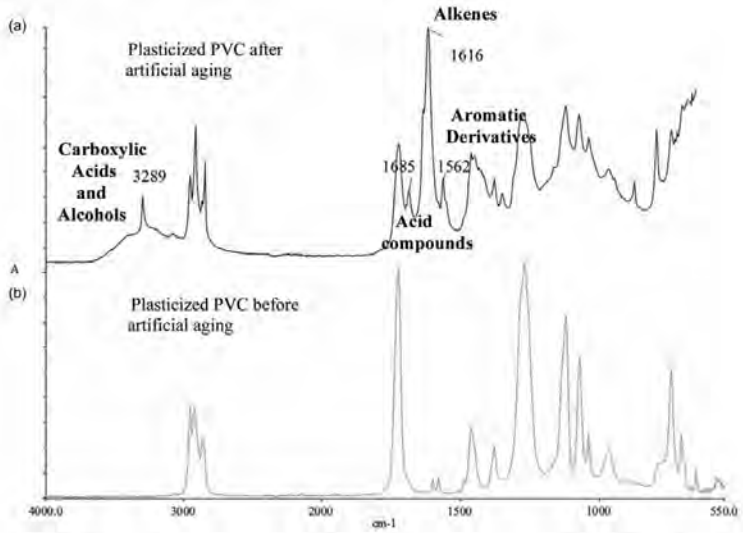

FIG. 2. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra from the degradation layer formed on the plasticized poly(vinyl chloride) (PVC) surface after artificial aging (a) and the plasticized PVC extracted from the sample (b).

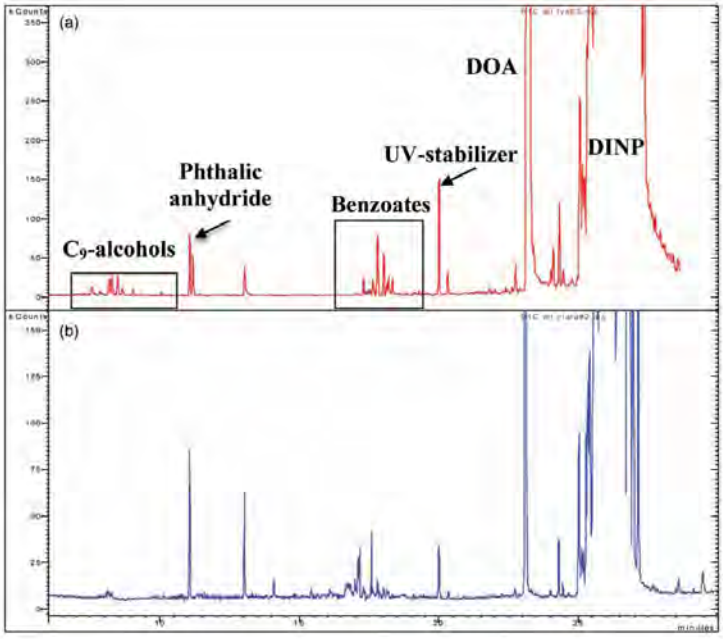

FIG. 3. Total Ion Chromatograms from gas chromatography-mass spectrometry (GC-MS) analysis of the photolysis products isolated from the commercial plasticized poly(vinyl chloride) (PVC) after artificial aging (a) and the plasticizer extracted from the unaged commercial PVC (b).

TABLE 2. SOLUBILITY PARAMETERS OF PVC POLYMER AND SOLVENTS USED IN CLEANING TREATMENTS

Solubility parameter ($MP^{1/2}$)	
Water*	48.0
Ethanol*	26.2
Propanol *	24.9
Heptane*	15.3
Poly(vinyl chloride)**	20.2

*Values taken from Burke (1984).
**Value taken from Wilkes *et al.* (2005).
PVC, poly(vinyl chloride).

Unlike the PVC polymer, plasticizers have a pronounced hydrophobic character and are rather soluble in organic solvents (Hutzinge and Staples 2003). For this reason, a quantitative study was additionally performed to test the suitability of the organic solvents selected for the cleaning process with respect to the plasticizers contained within the commercial PVC (see Section 3.3).

Despite the polarity of the C–Cl bonds in the PVC, the addition of plasticizer to its formulation provides hydrophobicity to the polymer (Kuisma 2006), which impedes the flow of aqueous solutions on the surface and leads to less efficient cleaning due to the reduced contact between the plastic surface and the aqueous cleaning solutions. Given that detergents are able to decrease the water surface tension and subsequently diminish the contact angle between the water and a hydrophobic surface, two detergents were included for testing on the plasticized PVC. The first detergent proposed was Dehypon LS45, a non-ionic surfactant already recommended for the cleaning of plastic works of art (Huys and van Oosten 2005; Shashoua 2008). The second detergent selected was Hostapon T, which has not been specifically indicated for plastics cleaning but its use is common in textiles conservation (Fields *et al.* 2004). Dehypon LS45 is composed of a ethoxylated and propoxylated fatty alcohol (Huys and van Oosten 2005) and it is partially miscible in water (20°C) (Fields *et al.* 2004) while Hostapon T is an anionic surfactant composed of fatty acid methyl tauride with sodium salt (64%) and soluble in water (150 g dm^3 at 20°C).

When organic material from fingerprints and oily substances are accumulated or encrusted inside porous or rough surfaces, the use of detergent solutions, organic solvents, or even mechanical methods may produce insufficient results. In these particular cases, a solution 1 mol dm^{-3} of KOH in water has been proposed by some researchers for the clean-up of PVC (Casati *et al.* 2000). In order to test the safety of this solution when cleaning plasticized PVC artworks, 1 M aqueous KOH was included in the current investigation.

Apart from aqueous solutions, solvents, and detergents, commercial cleaners specifically formulated for plastic objects are sometimes considered for plastics cleaning in the conservation field. However, the chemical information relating to these products is limited or non-existent, which can create doubts about their safety on plastic art objects. In order to gather more information about the behavior and suitability of these plastic cleaners, a commercial cleaner (Brillianize-Kleenmaster) recommended for plastic works of art was included for testing. This cleaner is composed of 83% water and 17% of unspecified compounds and it has been used by some conservators specialized in plastic works of art. Finally, a commercial cleaner formulated for domestic use (Multiren, composed of isopropanol, ethanol, and unspecified anionic surfactants) was also examined in order to compare the results obtained from this commercial multi-use cleaner to those obtained from the specifically designed for plastic art objects.

2.3 CLEANING TREATMENT PROTOCOL

The cleaning treatments were performed on the surface of PVC film samples of approximately 2 × 2 cm at room temperature using commercial cotton swabs, which were chosen to make the procedure easily replicable and similar to those normally applied by conservators (Budden 1991; Huys and van Oosten 2005). Damp cotton swabs with any excess liquid drained off were gently rolled in circles over the plastic surface, consistently following the same pattern of movement. As the cleaning solvents used have different boiling points, the cleaning was performed with brief, rapid applications in order to avoid differences in the evaporation rates and achieve consistent contact time between all of the cleaning solutions and the surface. For this purpose, the cotton swabs were replaced every 5 seconds. The cleaning agents were applied for a total of 100 seconds. The exception to this procedure was the application of the commercial cleaning agents, which had specific directions for their use. Those procedures, along with the one for using the other cleaning agents, are described in table 1.

2.4 EVALUATION OF TREATMENT RESULTS

The results of the cleaning treatments were assessed qualitatively and quantitatively. Qualitative assessments were done with visual examination under magnification, assessing the change in color or gloss and estimating the amount of remaining surface deposits and the presence of any residues. The sensitive detection of residues left on the surface, chemical alterations, and plasticizer extraction was done by examination of the ATR-FTIR spectra measured

before and after the treatments, focusing on changes in the absorption bands associated with the plasticizers. Since ATR-FTIR analyses have a sample penetration of a few microns, corresponding to the wavelength of the incident beam (Coombs 1999), the information obtained is predominantly related to the surface, where the cleaning process takes place. An additional advantage of the ATR-FTIR spectroscopy over other techniques is that samples do not need any preparation, and thus there is no interference between the treatments and reactant used to prepare the sample and the results obtained by the cleaning.

The assessment of plasticizer leaching from the bulk polymer could not be done directly using the chosen infrared spectroscopy method. The penetration of the cleaning agents into the bulk could not be measured by ATR-FTIR spectroscopy, as this is a surface analysis technique. Therefore, the tendency to absorb cleaning agents into this particular plastic material was assessed by weight gains (indicating absorption) or losses (indicating leaching) after immersion, using a procedure proposed by Sale (1988) described in detail in the Appendix. The results of this testing are shown in table 3. The sample's weight after water immersion remained steady at 2 minutes of immersion, but started to increase measurably after 2 hours. In contrast, the weight of the samples immersed in ethanol and propanol significantly decreased (beyond the standard deviation of the measurement) after 2 minutes of immersion, and this weight loss continued until the end of the experiment. Therefore, under the experimental conditions described in this research (cleaning treatments performed with damp cotton swabs in 5 seconds sequences up to a maximum of 100 seconds), the absorption of deionized water, ethanol, and propanol was judged to be negligible during the cleaning processes. However, weight decrease after ethanol and propanol immersions was interpreted as a leaching of plasticizer from the samples, and that process was investigated further in more detail.

The quantitative study of the plasticizer loss required a reliable measure of the plasticizer content in the material and its interaction with the polymer and cleaning agent. The quantitative analyses were focused on the measurements of plasticizer and not on other additives in the samples, because the plasticizers were the main additives detected in the plasticized PVC composition and their loss critically affects the plasticized PVC lifetime by altering the mechanical and physical qualities in the material. By contrast, UV and heat stabilizers were not considered in this study due to the small percentage in the material composition, although their removal could also alter important properties of the plastic at a big timescale.

TABLE 3. PLASTICIZED PVC SAMPLE WEIGHTS BEFORE AND AFTER IMMERSION

	Water			Ethanol			Propanol		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Before immersion	325.6 ± 0.1	351.5 ± 0.2	350.4 ± 0.2	348.8 ± 0.1	351.3 ± 0.1	339.3 ± 0.2	337.6 ± 0.1	335.9 ± 0.0	335.6 ± 0.0
2 Minutes immersion	325.9 ± 0.0	351.6 ± 0.0	350.5 ± 0.1	347.4 ± 0.1	350.0 ± 0.1	337.9 ± 0.2	336.2 ± 0.1	333.8 ± 0.1	334.1 ± 0.1
2 Hours immersion	325.8 ± 0.1	351.8 ± 0.2	350.7 ± 0.1	344.8 ± 0.1	347.6 ± 0.1	336.0 ± 0.2	330.9 ± 0.2	331.9 ± 0.2	330.8 ± 0.2
24 Hours immersion	326.1 ± 0.1	351.9 ± 0.1	350.9 ± 0.0	338.9 ± 0.1	342.2 ± 0.1	331.1 ± 0.1	324.8 ± 0.1	322.4 ± 0.1	323.3 ± 0.2

Plasticized PVC samples' weight in milligrams recorded before and after specific immersion 3 times in deionized water, ethanol 99.9%, and 1-propanol 99.5%. Standard errors are indicated beside the weight values.
PVC, poly(vinyl chloride).

Plasticizers are bound to the PVC matrix through weak physical attractive forces (Williams 1993) and thus they can be extracted by solvents in contact with the polymer. This process is controlled by the solvent–plasticizer compatibility and the solvent–PVC polymer compatibility (Hutzinge and Staples 2003), which means that the plasticizer will be extracted if it is highly soluble in the solvent or poorly compatible with the polymer matrix. The plasticizer's compatibility with PVC has been described in terms of the ratio CH_2/C=O in the plasticizer, as both low and high ratios would make the PVC polymer not very compatible with the plasticizer (Tiemblo *et al.* 1995). In the samples used in this study, the ratio CH_2/C=O could be calculated from nuclear magnetic resonance data (provided by Riso-DTU National Laboratory, Denmark) and was found to be 4.2, an intermediate value indicating a high compatibility between the plasticizer mixture and the PVC polymer. However, despite the high compatibility of plasticizer with PVC polymer in this commercial material, the gravimetric study of the plastic after immersion in organic solvents demonstrated significant plasticizer extraction. The pure aliphatic structure of the adipate compound, DOA, a minor constituent of the plasticizer mixture, also facilitates its migration, hence its extraction (Marcilla *et al.* 2007).

For the study of the plasticizer migration, ATR-FTIR spectroscopy was used, as unlike other techniques used for the same purpose, such as weight loss (Sale 1988), chromatography (Messadi *et al.* 1981), radioactivity (Duvis *et al.* 1991), or infrared spectroscopy (Murase *et al.* 1994), ATR-FTIR provides noteworthy advantages. For instance, it is possible to perform the analysis immediately after the cleaning processes and under normal working conditions in the laboratory, so important factors affecting the diffusion process, such as the solvent–PVC contact time and temperature, could be controlled and held constant. Other factors influencing the transport, such as plasticizer concentration (Messadi *et al.* 1981) and shape and size of plasticizer molecules (Wilson 1995), were assumed to be constant under the experimental conditions, and hence should not have affected the comparison of the cleaning agents.

Previous researchers have already quantified by relative methods the increase of carbonyl groups on PVC-composed materials during artificial aging (Mantuana and Kamdem 2002). Based on these studies, the decrease rather than the increase of the plasticizer carbonyl band in the PVC sample in this study was quantified during the cleaning processes. For this purpose, a "Plasticizer Index" (PI) was calculated (Stark and Matuana 2004) as the ratio of the peak intensities of the plasticizer carbonyl band and the PVC C–H band before and after the cleaning treatments (*Eq. 1*). Thus, the PI indicates the percent of plasticizer lost from the sample surface due to extraction during the cleaning treatment. As the PI represents plasticizer loss, PI values are expressed as negative numbers:

$$\mathrm{PI}(\%) = \left[A\left(1722\ \mathrm{cm}^{-1}/1426\ \mathrm{cm}^{-1}\right)_{\mathrm{Aftercleaning}} - A\left(1722\ \mathrm{cm}^{-1}/1426\ \mathrm{cm}^{-1}\right)_{\mathrm{Beforecleaning}}\right] / A\left(1722\ \mathrm{cm}^{-1}/1426\ \mathrm{cm}^{-1}\right)_{\mathrm{Beforecleaning}} \times 100 \quad (1)$$

As PI values are calculated relative to the starting plasticizer content, it is not necessary to know the exact plasticizer concentration in the sample. This makes the PI replicable and comparable in any plasticized polymer surface.

Following *Eq. 1*, an initial pilot experiment showed that after 10 seconds cleaning with di-isopropyl ether (an excellent plasticizer solvent), the PI dropped as a consequence of plasticizer extraction, and progressively increased by replacement from plasticizer migrating from the bulk (fig. 4). This finding demonstrated that data obtained from spectra recorded at different times after the cleaning performance could not be compared due to the plasticizer migration. Therefore, in order to maintain the repeatability of the method, the ATR-FTIR spectra were recorded at a fixed time after the cleanings' execution. For practical reasons a time of 1 minute was chosen, given that it was the shortest time that allowed for correct placement of the sample in the ATR cell.

Once the time interval for taking measurements after the cleaning treatment was defined, the treatments with all cleaners were done at 10, 30, 50, 100, and 150 seconds. The distribution of the plasticizer in the PVC

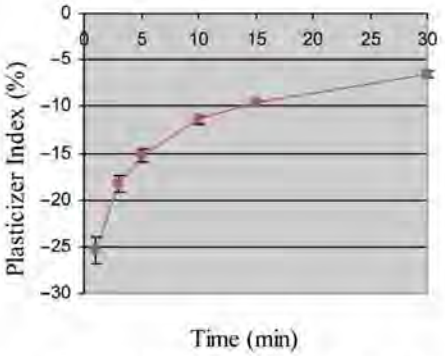

FIG. 4. Plasticizer Index (%) after 1, 3, 5, 10, 15 and 30 minutes following the 10 seconds. cleaning treatment with di-isopropyl ether. Error bars show the standard deviations of the means calculated from five measurements.

sheet was initially estimated by the absorbance ratio plasticizer/PVC. Fifteen points were randomly measured on the PVC surface and two independent absorbance bands were selected for the ratio calculations: the plasticizer carbonyl band or C=O stretching vibration, that was identified at 1722 cm^{-1} in the plasticized PVC spectrum, and the PVC methylene band at 1426 cm^{-1}, which is characteristic of the PVC polymer (Tabb and Koenig 1975) and thus could be used as an internal reference to normalize the results. The ratio $A_{C=O}/A_{CH_2}$ was measured to be 7.7 ± 0.6 and 88% of the measurements lay within the standard deviation of the mean. This demonstrated that the plasticizer was reasonably homogeneously distributed on the PVC surface, making it possible to perform relative quantifications without exhaustive averaging over different locations. A PI value was calculated for each cleaning agent from three replicate treatments performed at each determined cleaning time.

3. Results and Discussion

3.1 Cleaning of unaged PVC samples

ATR-FTIR spectra collected from 100-second treatments with each cleaning solution were compared with the spectrum of plasticized PVC prior to the cleaning (figs. 5–7). As presented in fig. 5b, several changes were observed in the plasticized PVC spectrum after cleaning with 5% aqueous Dehypon LS45: the plasticizer C–O bands at 1125 and 1073 cm^{-1} underwent broadening and overlapping, and the CH_2 and CH bands from PVC and plasticizer at higher frequencies in the spectrum increased their intensity. These changes in the plasticized PVC spectrum corresponded to the superposition of both Dehypon LS45 and plasticized PVC bands, due to the incomplete removal of the detergent after rinsing with deionized water. On the contrary, no changes were observed in the plasticized PVC spectrum when 5% aqueous Hostapon T was used (fig. 5d). Unlike Hostapon T, the detergent solution 5% aqueous Dehypon LS45 required a repetitive rinsing with deionized water in order to clear it from the PVC surface during the execution of the cleaning. This was probably caused by the partial solubility of Dehypon LS45 in water, which makes the elimination of the product difficult. Therefore, absorption peaks associated with the detergent were still detected in the plasticized PVC spectrum after the cleaning.

The use of deionized water did not modify the plasticized PVC spectra (fig. 6b) but a severe alteration of the plasticized PVC spectrum was observed when pure organic solvents propanol (fig. 6c), ethanol (fig. 6d), and heptane (fig. 7b) were used: the plasticizer C–H band at 1460 cm^{-1} decreased its intensity relative to

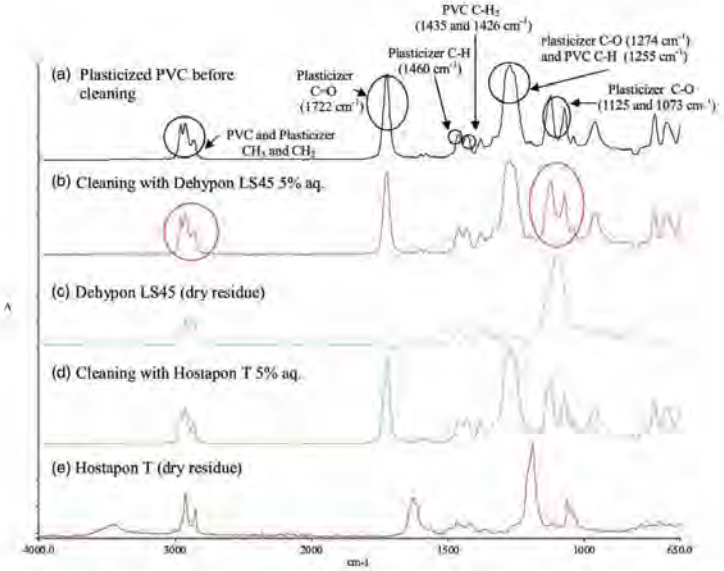

Fig. 5. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the plasticized poly(vinyl chloride) (PVC) surface before cleaning (a) and after 100 seconds cleaning treatments with: 5% aqueous Dehypon LS45 (b); 5% aqueous Dehypon LS45 (dry residue) (c); 5% aqueous Hostapon T (d), and 5% aqueous Hostapon T (dry residue) (e). Red circles indicate spectral regions where modifications of the plasticized PVC spectra occurred.

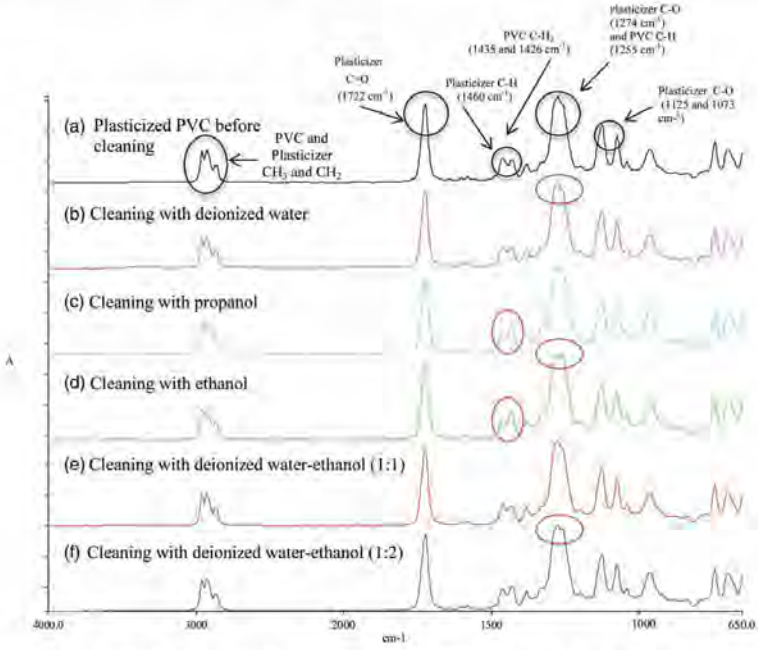

FIG. 6. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the plasticized poly(vinyl chloride) (PVC) surface before cleaning (see interpretation of absorption bands on fig. 2a) (a) and after 100 seconds cleaning with: deionized water (b), 99.5% isopropanol (c), 99.9% ethanol (d), water-ethanol (1 : 1 v:v) (e), and water-ethanol (1 : 2 v:v) (f). Red circles indicate spectral regions where modifications of the plasticized PVC spectra occurred.

the PVC CH_2 bands at 1435 and 1426 cm^{-1} (figs. 6c, 6d, 7b), and the profile of the band formed by the overlapping of the plasticizer C–O band at 1274 cm^{-1} and the PVC C–H band at 1255 cm^{-1} was modified (figs. 6c, 6d, 7b).

A 1 : 1 v:v water–ethanol mixture caused no change in the plasticized PVC spectrum (fig. 6e), but modification of the overlapped plasticizer 1274 cm^{-1} and PVC 1255 cm^{-1} bands was noticed when the 1 : 2 v:v mixture was tested (fig. 6f), as was observed in the case of the pure organic solvents. Neither modification of the spectrum nor residues from the basic 1 M KOH solution (fig. 7c) and the commercial products Brillianize-Kleenmaster and Multiren was detected after cleaning (figs. 7d, 7f).

3.2 CLEANING OF ARTIFICIALLY AGED SAMPLES

According to the results on unaged plasticized PVC samples, deionized water, 1 : 1 v:v deionized water–ethanol mixture, 1 M aqueous KOH, Multiren, 5% aqueous Hostapon T, and Brillianize-Kleenmaster were found to be effective and safe for plasticized PVC cleaning. As a result, these cleaning solutions were tested on degraded samples to evaluate their effects on that material.

Visual examination of the samples treated with these cleaning agents indicated the same result: the surface became visibly clearer. However, ATR-FTIR spectroscopy (figs. 8, 9) and optical microscopy (fig. 1) showed significant differences between the cleaners' actions. No peaks from the degradation products were visible on the plasticized PVC spectrum after cleaning with 5% aqueous Hostapon T (fig. 8b). However, low intensity peaks corresponding to the degradation layer components remained in the ATR-FTIR spectrum after cleaning with KOH solution (fig. 9b), and strong peaks from degradation products were detected after cleaning with the deionized water (fig. 8c), deionized water–ethanol mixture (1 : 1) (fig. 8d), Multiren (fig. 9c), and Brillianize-Kleenmaster (fig. 9d). Optical microscopy results essentially matched with the interpretations of the ATR-FTIR spectra. Significant amounts of the degradation products were visible in the photomicrographs after cleaning with Multiren (fig. 1f), Brillianize-Kleenmaster (fig. 1h), water and water–ethanol mixture (1 : 1) (fig. 1c, 1d, respectively) and 1 M aqueous KOH solution (fig. 1e),

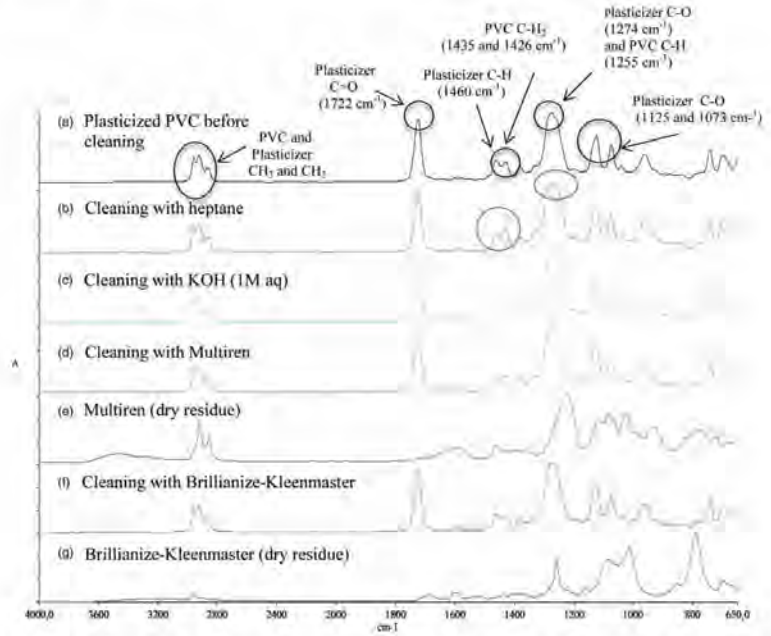

FIG. 7. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the plasticized poly(vinyl chloride) (PVC) surface before cleaning (see interpretation of absorption bands on fig. 2a) (a) and after 100 seconds cleaning with: heptane (b), 1 M aqueous KOH (c), Multiren (d), Multiren (dry residue) (e), Brillianize-Kleenmaster (f), and Brillianize-Kleenmaster (dry residue) (g). Red circles indicate spectral regions where modifications of the plasticized PVC spectra occurred.

while no residues were found after cleaning with the detergent solution Hostapon T (fig. 1g).

3.3 QUANTITATIVE ANALYSIS OF PLASTICIZER LEACHING

The PI values (accompanied by their standard deviations about the means) for all the cleaning agents applied to unaged plasticized PVC are shown in figure 10. The results demonstrate that deionized water and the 1 M aqueous KOH solution did not extract plasticizer, while all the organic solvents (ethanol, propanol, and heptane) extracted plasticizer during 10 seconds cleaning. Even though surfactant solutions have been recommended for plasticized PVC cleaning treatments (Fairbrass 1999, Shashoua 2008), significant differences were found in this study among the detergent solutions tested. It was observed that Dehypon LS45 seemed to extract plasticizer after 50 seconds of cleaning (although only to a minor extent in comparison with the organic solvents), while the detergent solution Hostapon T did not show evidence of plasticizer extraction at any cleaning time. Regarding the commercial products, both the specified cleaner for plastics in conservation (Brillianize-Kleenmaster) and the multipurpose cleaner (Multiren) showed similar behavior, with neither extracting plasticizer. In the case of the ethanol–water mixtures, the proportion 1 : 1 did not show any plasticizer extraction. By contrast, the proportion 1 : 2 ethanol–water mixture began to extract plasticizer after 50 seconds, but to a minor extent compared with pure ethanol. As figure 10 shows, the PI had varying values near zero in those cases in which the plasticizer was not extracted during the cleaning treatment. This variation could be due to slightly inhomogeneous distribution of the plasticizer in the PVC sheet, which would produce an erratic value of the PI. However, an additional explanation could be the poorly controlled mechanical action of the cotton swabs during the cleaning, which have been demonstrated to bring plasticizer from inner layers to the PVC surface when used for dry cleaning (Morales Muñoz 2010).

4. CONCLUDING REMARKS

From the methodology applied in this research, it has been shown that it is possible to demonstrate safe cleaning solutions for plasticized PVC, either unaged or in a degraded state. This is significant for museum

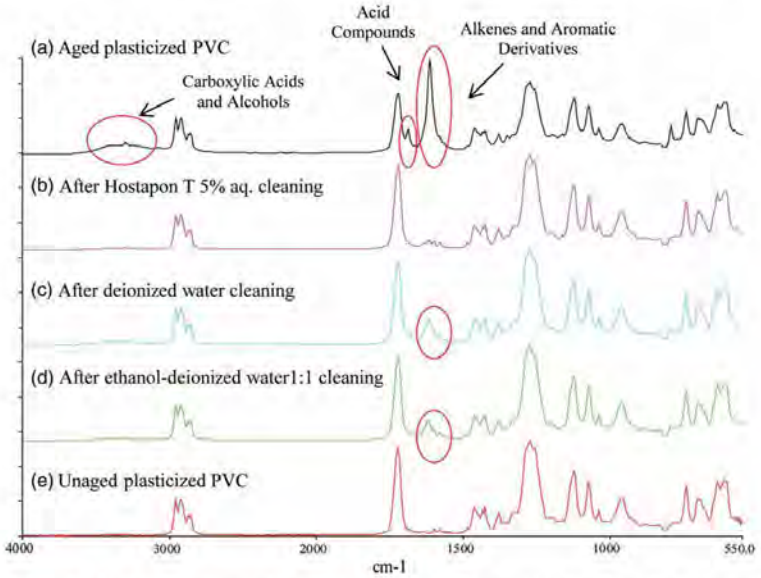

FIG. 8. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the plasticized poly(vinyl chloride) (PVC) surface after artificial aging (a), and after artificial aging and 10 seconds cleaning with: 5% aqueous Hostapon T (b), deionized water (c), and ethanol–deionized water 1 : 1 v:v (d). ATR-FTIR spectrum of the unaged plasticized PVC surface is shown in (e).

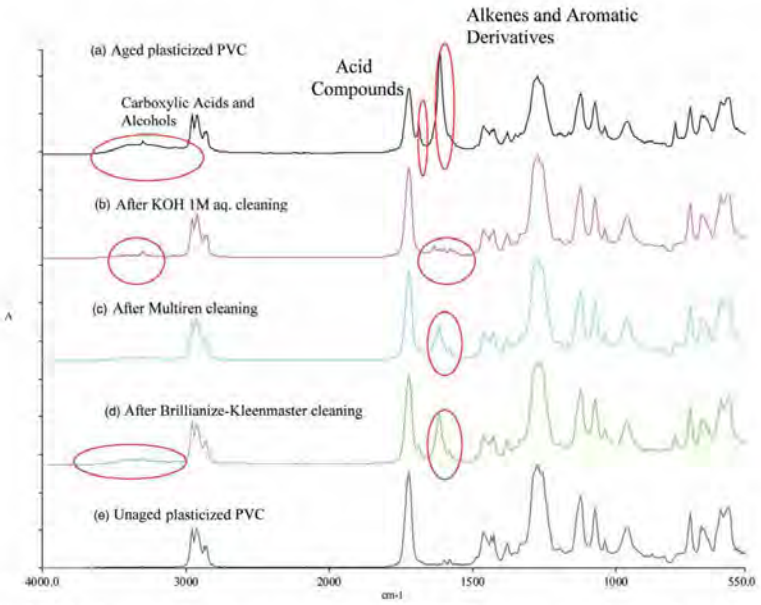

FIG. 9. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the plasticized poly(vinyl chloride) (PVC) surface after artificial aging (a), and after artificial aging and 10 seconds cleaning with: 1 M aqueous KOH (b), after cleaning with Multiren (c), and after cleaning with Brillianize-Kleenmaster (d). ATR-FTIR spectrum of the unaged plasticized PVC surface is shown in (e).

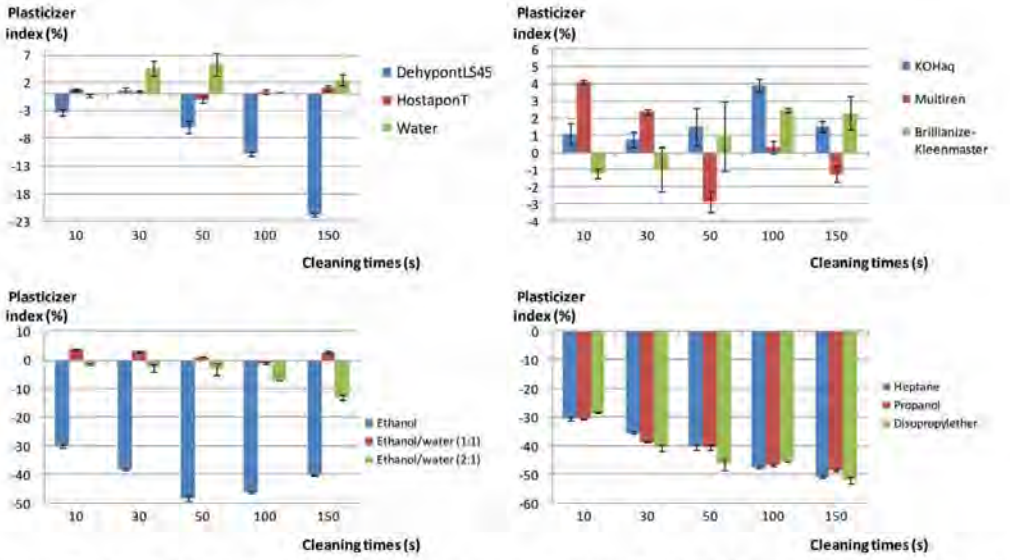

FIG. 10. Plasticizer Index (%) after cleaning for 10, 30, 50, 100, and 150 seconds with the cleaning agents. Error bars show the standard deviation of the means calculated from three measurements.

collections, since the development of cleaning treatments for plastic works of art in different conservation conditions is becoming an important concern.

It has been also demonstrated that despite the fact that only one of the commercial cleaners used in this study was specially formulated for plastics cleaning, no differences were found between their effectiveness. This suggests that commercial cleaners recommended for works of art are not always more effective or safer than other commercial cleaners formulated for more general use. Nevertheless, known cleaning formulations produce more predictable results than commercial cleaners, and the known formulations offer the possibility of tailoring the composition or proportions for the needs of a particular work of art.

Detergent solutions were also found to be suitable for plasticized PVC cleaning. However, the PI showed that some of the formulations might extract plasticizer from the PVC. Therefore it is recommended to test a selected detergent solution before using it on a plasticized PVC object. Furthermore, it was found that organic solvents extracted plasticizer at all of the cleaning time durations, so it may not be appropriate to use pure organic solvents on plasticized PVC for any type of cleaning. On the contrary, mixtures of organic solvents with deionized water may be considered, since they seemed not to extract plasticizer when used in certain proportions.

One of the goals of this research was not only to identify suitable cleaning agents for undegraded plasticized PVC, but also to find effective cleaning solutions to remove degradation products in a way that did not extract the plasticizer from the bulk material. Among the cleaning agents considered suitable (i.e., which were safe in terms of plasticizer extraction) for this particular sample of undegraded plasticized PVC, detergent solutions provided good cleaning results in removal of the photo-degradation products that appeared on the plasticized PVC surface after artificial aging.

Finally, the PI developed during this research was found to be a useful tool for the selection of suitable water–organic solvent mixtures, providing quantitative measures to determine cleaning times and mixture compositions that neither extracted plasticizer nor caused modifications of the plasticized PVC spectrum. This approach may be considered as additional to the Hildebrand parameters to calculate solvent mixtures, providing results in real time for the plasticized PVC samples. Because of the repeatability of the methodology, the PI may be applied to the cleaning of other plasticized PVC compositions and additional cleaning mixtures.

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Appendix

The artificial aging of the plasticized PVC was achieved through exposure in an ATLAS CI 3000+ Weather-O-Meter operating with medium-high temperature conditions. In this device the light source was a 1.97 kW xenon lamp using Type S borosilicate inner and outer filters. The lamp and filters selected were those that reproduced outdoor daylight conditions. The irradiance level was 50 W m^{-2} (at 300–400 nm) and the air temperature in the chamber was set at the minimum allowed for the irradiance conditions, 46°C. The black panel standard temperature was 61 ± 1°C and the relative humidity was 54 ± 1%. The samples were exposed until the surface reached high levels of degradation, which required 672 hours.

In this study, the degradation products created by accelerated aging were analyzed by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometry and gas chromatography-mass spectrometry (GC-MS), and the former technique was also used to assess the results of the surface cleaning treatments. An ATR-FTIR spectrometer (Perkin Elmer Spectrum One) equipped with a diamond/ZnSe cell was employed for the analysis of the unaged and aged sample surfaces before and after cleaning. The spectra were recorded in the 650–4000 cm^{-1} range, at a resolution of 8 cm^{-1} and averaging 20 scans. The spectra were analyzed without smoothing or base line corrections and no other corrections were applied to the spectra. For the GC-MS analyses a Varian 3400 gas chromatograph interfaced to a Saturn II ion trap mass spectrometer was used. The photo-degradation products were separated using a 0.32 mm i.d. × 30 m WCOT (Wall-Coated Open-Tubular) fused silica column coated with VF-23ms, or alternatively coated with CP-SIL 8CB at a thickness of 0.25 µm (Analytical, Denmark). Separation of a wide range of products was achieved using a temperature gradient from 50 °C to 250 °C. Full mass spectra were recorded every 0.5 seconds. Degradation products were identified using a NIST search engine and authentic standards. Sample derivatization was not used for the analyses.

Nuclear magnetic resonance (NMR) spectra were obtained on a 500 MHz Bruker Avance 2 NMR spectrometer, and this method was used to analyze a plasticizer sample isolated from the PVC material. Both ^{1}H and ^{13}C spectra were recorded using a $CDCl_3$ solution with TMS as reference for chemical shifts. The distortionless enhancement of polarization transfer technique was applied to the spectrum recorded with a 135° flip angle in order to determine the multiplicity of carbon substitution. The ratio CO/CH_2 was determined by integration of the ^{1}H spectrum.

Inorganic additives in the plasticized PVC sheets were quantified by XRF using a Philips PW 2400 and UniQuant ver. 5.49. Detection limits were estimated to be 0.001–0.002% and calibration was performed using the pure elements. X-ray fluorescence analysis was outsourced to Danish Technological Institute (Aarhus, Denmark).

For the XPS analyses, an X-ray photoelectron spectrometer system Thermo Scientific K-Alpha was used to study the plasticized PVC samples and characterize the samples nondestructively for elemental and chemical state information. Samples were mounted on a standard sample holder and analyzed using the micro-focused, monochromatic Al Kα X-ray source. The size of the X-ray spot was chosen by the operator to match the sample and analysis type (spot sizes between 30 and 400 µm may be selected on this instrument). The instrument's charge compensation system was employed during analysis.

The results of the cleaning treatment were evaluated visually and at 25×magnification, using an Axiotech 100HD optical microscope. The determination of the amount of cleaning agent absorbed into the bulk PVC samples was done according to a method described previously (Sale 1988). Plasticized PVC samples of 1 × 1.5 ± 0.05 cm were placed in a desiccant chamber and weighed with 0.1 mg precision until constant weight was achieved. Samples were then put into glass vials, which were then filled with 4 ml of deionized water, 99.9% ethanol, or 99.5% 1-propanol. Three replicate samples were prepared for each solvent and kept in the laboratory in the sealed vials at room temperature. Each sample was removed from the vials after 2 minutes, 2 hours, and 24 hours of immersion, blotted dry with filter paper in order to remove the solvent absorbed on the surface, and weighed. An average taken from three measurements was recorded per sample before and after the immersions.

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Further Reading

Morales Muñoz, C. 2011. Spectrocolorimetric and microscopic techniques for the evaluation of plasticized PVC cleaning: a case study applicable to three-dimensional objects at museums. *Journal of Microscopy* 242: 257–66.
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Sources of Materials

Plasticized PVC sheets (Product ref: 109200)
Vink Plast ApS
Kristrup Engvej 9
DK-8960 Randers
Tel. 89 11 01 00
Fax 86 41 58 90
E-Mail: info@vink.dk
http://www.vink.dk

Ethanol, anhydrous 99. 9%
De Danske Spritfabrikker
C. A. Olesens Gade 1
9000 Aalborg
Denmark
1-Propanol 99.5%

Prolabo
VWR International ApS
Valhøjs Alle 174-176
2610 Rødovre
Denmark
Tel: +45-43868788
E-mail: info@dk.vwr.com

Heptane 98%
Kebo Lab
Struers Kebo Lab A/S
Roskildevej 16, DK-2620
Albertslund
Tel: +45-43868788

Deionized water obtained using a Millipore Elix Water Cleaning System
EMD Millipore, a division of Merck KGaA,
Darmstadt, Germany
Telephone: 1-800-MILLIPORE (+1 800-645-5476)
http://www.emdmillipore.com

Hostapon T 5% aqueous
Clariant GmbH c/o Chemlink Specialities Ltd.
Gladstone house, 26-30 Station Road
Urmston
Manchester M41 9JQ
Tel: 44-0-161-629-2129
http://www.chemlink.co.uk

Dehypon LS45 5% aqueous
Cognis GmbH
c/o Care Chemicals, Henkel Organics

KOH 1M aqueous
J.T. Baker

Brillianize-Kleenmaster
The Brillianize Company
4952 Industrial Way
PO Box 867
Benicia, CA 94510
Tel: (707) 751-0656
http://www.brillianize.com

Multiren
Multi-Drik
Available in supermarkets

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7. APPLICATION TO REAL SAMPLES

In order to provide a better understanding of cleaning methods on plasticized PVC, the results obtained from the investigation of dry and wet cleaning methods on plasticized PVC testing material were tried on a real plasticized PVC object. The selected object was an old doll made of plasticized PVC that presented signs of degradation and dirtiness.

The main purposes targeted were:

a) Examination of the efficiency of dry and wet cleaning methods on a real plasticized PVC object, considering both non-degraded and degraded surfaces;

b) Examination of the effects caused by wet cleaning methods on a real plasticized PVC object, considering both non-degraded and degraded surfaces;

c) Investigation of quantification methods of the cleaning efficiency on a real plasticized PVC objects;

d) Investigation of quantification methods of the cleaning efficiency on 3D objects.

7.1. Spectrocolorimetric and microscopic techniques for the evaluation of plasticized PVC cleaning: a case study applicable to three-dimensional objects at museums"

C. Morales Muñoz.

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Spectrocolorimetric and microscopic techniques for the evaluation of plasticized PVC cleaning: a case study applicable to three-dimensional objects at museums

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Researcher, Spain

Key words: Non-contact profilometry, plasticized PVC, plasticized PVC cleaning, plastics conservation.

Summary

For the validation of a cleaning method in conservation, the examination of the object's surface after the cleaning and the quantification of the cleaning efficiency are significant steps. In this study, several cleaning solutions were tested on a plasticized poly(vinyl chloride) object whose surface was characterized before and after cleaning by optical microscopy and noncontact profilometry. In addition, different methods to quantify the cleaning efficiency based on spectrocolorimetric and microscopic techniques were provided. The results showed that noncontact profilometry supported by optical microscopy and spectrocolorimetry was very useful for the characterization of the plasticized poly(vinyl chloride) surface before and after the cleaning and also for the determination of the cleaners' efficiency.

Introduction

The cleaning process of an artwork necessarily involves the examination of the object's surface and the quantification of the cleaning efficiency. However, there are additional difficulties when cleaning plastics surfaces, due to their chemical complexity, and when cleaning three-dimensional (3D) objects, due to their irregular morphology and sometimes large dimensions. In art conservation, some studies have focused on the cleaning of plasticized poly(vinyl chloride) (PVC), proposing several cleaning solutions or solvents for the cleaning of soiled PVC surfaces (Fairbrass, 1999; Huys & van Oosten, 2005) and examining the surface after the cleaning (Fairbrass, 1999). However, none of this research has extensively study the chemical and physical effects of the cleaning, nor compared dry methods with cleaning solutions and quantified the cleaning efficiency. Furthermore, the use of profilometric techniques for the cleaning assessment has been used on bidimensional samples from PVC (Fairbrass, 1999), plastic floor (Kuisma *et al.*, 2003), paintings (Wei *et al.*, 2005) or photographs (Ravines, 2008), but only techniques as 'conoscopic holography' (Carcagnì *et al.*, 2009), which provides more limited and inaccurate information than microscopic techniques, has been *in situ* applied to 3D objects.

Differently from scanning electron microscopy (SEM), optical microscopy and atomic force microscopy (AFM), profilometry provides 3D images that help conservators to better understand topography of surfaces. In addition, quantitative values not achieved by means of the other techniques are calculated by the profilometer equipment. For the examination of 3D objects, optical microscopes are currently available with no sampling or size restriction. Similarly, the new portable profilometer equipment used in this investigation does not have any size or shape restriction when examining the sample object and may be used over the original surface without need of sampling from the object. Profilometry has an advantage over the optical microscopy in providing *in focus* images from rough and uneven surfaces (Lange *et al.*, 1993). On the contrary, SEM technique needs of sampling from the object, which is not always easy or possible when examining an artworks. Nevertheless, the versatility of the SEM technique is not achieved by profilometry or optical microscopy, from which no chemical information is obtained. When compared to other 'portable rugosimeters', as conoscopic holography (Carcagnì *et al.*, 2009), both profilometry and conoscopic holography consist of noncontact devices and permit on-site analyses. However, an advantage of the conoscopic holography is the roughness imaging of areas as large as 17×20 mm^2 on plane surfaces (Carcagnì *et al.*, 2009), whereas profilometric is restricted to smaller areas depending on the objective's resolution. However, this limitation is solved by an additional application in the profilometer software that allows the 'stitching' of several scans from adjoining surface's areas (Van Den Berg *et al.*,

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2008). In addition, conoscopic holography is limited to surface roughness evaluation and does not supply quantitative values of roughness.

In the particular case of plasticized PVC, it is worth mentioning the fact that some artworks composed of this type of plastic are performed by using extremely flat and smooth PVC surfaces, what makes 2D imaging techniques as microscopy or SEM inappropriate to detect any change on the topography of the material (Morales Muñoz, 2010). With a resolution of nanometres, profilometry overcomes this problem by providing accurate 3D images and quantitative roughness parameters. However, and under a more practical point of view, microscopic techniques are at present more accessible and inexpensive than profilometry.

In summary, the main aim of this work has been to continue assessing on the cleaning of plasticized PVC surfaces (as a continuation of previous works, Morales Muñoz, 2010; Morales & Egsgaard, 2011) and to introduce a new method for the cleaning examination and quantification of 3D objects. For this purpose, mobile noncontact profilometry and optical microscopy techniques were proposed for the surface examination of a plasticized PVC object (an old doll made of plasticized PVC) after several cleaning treatments. As well, spectrocolorimetry and again noncontact profilometry served for the quantification of the cleaning efficiency. At last, a detailed identification of the doll components and an extended chemical investigation of the cleanings effects and efficiency have been already addressed in previous work (Morales & Egsgaard, 2011).

Materials and methods

Samples and cleaning methods

The head of an old doll from the 1970s and composed of plasticized PVC was used in this investigation. Although this doll lacked any artistic or historical value, it was made of a representative material within the plastics typically found in museums objects (Shashoua, 2001). GC-MS analyses from the doll showed that the PVC was plasticized with bis(2-ethyl-hexyl)phthalate and lubricated with 2-ethyl-hexyl esters of the fatty acids C12:0, C14:0, C16:0 and C18:0 (Morales & Egsgaard, 2011). In addition, the corresponding free acids were found in the doll composition although it could not be determined if they corresponded to lubricants or degradation products from the esters hydrolysis. The doll samples showed dirt embedded in the surface which was identified with organic materials usually founded in art objects as protein substances, fatty acid or polysaccharides, which are part of fingerprints, sweat, skin flakes, etc. Even though some authors have warned about the use of organic solvents for cleaning of museum objects (Sale, 1988), the type and area of dirt in the doll's surface made the use of dry cleaning methods ineffective and only wet treatments could be used (Morales & Egsgaard, 2011). The cleaning solutions proposed were: deionised water (Millipore®), mixture of ethanol and deionised water (1:1), 5% aqueous solution Hostapon T® (anionic surfactant composed of fatty acid methyl tauride sodium salt) (Weston, 1980), aqueous solution KOH 1M (strongly basic, pH 14) and Brillianize® (commercial cleaner for plastics artworks, composed of 83% water).

After several trials to determine the most suitable cleaning time for the doll surface, cleaning solutions were applied during 10 s by means of cotton swabs. Two cotton swabs were used for each cleaning solution in consecutive 5 s intervals. The damp cotton swabs were softly rolled on the doll surface by round movements in the same direction. Four replicate cleanings were carried out with each cleaner on areas of approximately 5 mm^2. The water and water–ethanol solutions were dried after cleaning with new cotton swabs; the Hostapon T® solution was rinsed with deionised water and dried with new cotton swabs, and Brillianize® was applied following the cleaner's recommendations which suggested wiping off the product with cotton swabs after its application. The doll cleaning was performed under normal laboratory conditions to reproduce common cleaning treatments at conservation studios or museums. Therefore, the environmental conditions were those usually used during restoration processes and no variations in the humidity or temperature were considered to affect the cleaning process of the doll.

Techniques description

The examination by optical microscopy was performed on samples taken from the base of the doll's head. On the contrary, no sampling was required for noncontact profilometry and spectrocolorimetry measurements, which were directly performed on the cleaned areas. Random points were measured before and after the cleanings in several areas of the doll. This procedure supposed a longer time in the analysis performance, especially when using the profilometer, but it provided information from different locations at the entire doll's surface and it did not restrict the results to specific spots.

Micrographs were obtained with an optical microscope Axiotech 100HD (Germany) at 12.5× magnification, whereas a portable spectrophotometer Minolta CM 2600D (Japan) equipped with a Standard Illuminant D65 (standardized daylight, 6500 K) was used for the lightness measurements (L^*), on an observation area of 3 mm diameter. Finally, a noncontact profilometer μsurf mobile provided by NanoFocus AG (Germany) and equipped with the μsoft software version 6.6 was used for the topographical analyses.

Mobile noncontact profilometry

A profilometer is essentially a confocal microscope that obtains a high number of images at different focal heights on the surface topography and creates a 3D image (Hamilton &

Fig. 1. Doll head being analysed in the profilometer μsurf mobile at Nanofocus AG in Germany.

Wilson, 1982; Lange *et al.*, 1993). The novelty of this work has been the use of a portable device that gives the advantage of measuring any area selected on an object without any shape or size restriction. Also, the equipment features give the possibility of transporting it to any location, which is indeed convenient for museums and conservation centres.

Different to other investigations (Fairbrass, 1999; Wei *et al.*, 2007; Van Den Berg *et al.*, 2008), the light source used in the profilometer was a green LED ($\lambda = 505$ nm) instead of white light (Fig. 1). LEDs, acronym for 'Light-Emitting Diode', are currently substituting classical white light bulbs in many types of equipment due to advantages like their small size and long life (Wessner, 2002). In addition, the short bandwidth of the green light used in the instrument reduced chromatical effects (personal communication with D. Hoffman from Nanofocus AG).

In this work, a 20× objective that measured areas corresponding to 0.8 × 0.8 mm^2 was used for the surface analysis (Wei *et al.*, 2005; Ravines et al. 2008; Morales Muñoz, 2010). A lower magnification objective 10× could have provided information from areas of 1.6 × 1.6 mm^2, although it had supposed a notable loss of resolution. The achievement of higher resolution could have been possible by means of 50×, 60× or 100× objectives in the mobile equipment, although this possibility was dismissed because the measuring field had been significantly smaller and therefore it would not be representative of macroscopic cleanings.

During the measurements, the step width in the *z*-direction was settled at 0.125 μm for both nontreated and cleaned surfaces measurements, what means that this value was the distance between the confocal images used by the profilometer to reconstruct the surface topography. Differently, 0.03-μm and a 0.08-μm-step widths were used when measurements with the same objective were carried out on smooth plasticized PVC samples (Morales Muñoz, 2011). These divergences in the step width used for the measurements are related to the surface's roughness. When measuring a smooth surface with a fine texture, a small step width is possible resulting in ultimate resolution. On the contrary, using a small-step width would not allow detection of any variation in the surface profile when a very rough sample is measured. Therefore, the step width selected in the *z*-direction is in practice what determines the resolution in the roughness measurements (Van Den Berg *et al.*, 2008).

Results and discussion

For the evaluation and quantification of the cleaning methods, optical microscopy, spectrocolorimetry and noncontact profilometry were used. These techniques were capable of detecting physical and visual variations corresponding to the removal of the black dirtiness present in the doll's surface, which has been chemically associated with lipids and protein compounds from finger prints, sweet and pollutants (Morales and Egsgaard, 2011).

Qualitative evaluation

Light microscopy was used to visualize the differences in the cleaning action produced among the cleaning treatments under the same procedure and cleaning time. Before the cleaning, black structures distributed all over the surface were clearly observed (Fig. 2a). After the cleaning with water, water–ethanol or Brillianize®, this black dirtiness was still visible (Fig. 2a, e, f), however no evidence were found when the KOH solution or Hostapon T® were used (Fig. 2b and c). Therefore, through the microscopic images

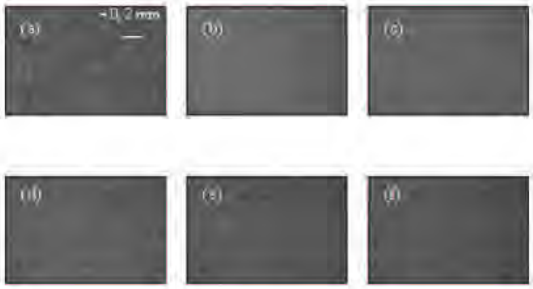

Fig. 2. Micrographs from the doll surface before cleaning (a) and after cleaning with: KOH 1M aq. (b), Hostapon T 5% aq. (c), deionised water (d), water–ethanol 1:1 (e) and Brillianize (f).

Hostapon T® and KOH solutions removed the dirtiness and provided the best results among the applied cleaners. On the contrary, the water–ethanol mixture and the commercial solution Brillianize® showed the poorest cleaning action. The dirtiness was partially removed with the deionised water, what evidenced an intermediate cleaning efficiency.

As in the micro pictures, the 3D images obtained through the noncontact profilometer showed significant differences on the doll's surface after the cleanings (Fig. 3). In general, the topography became more recognizable, what was associated with the removal of particles from the surface. However, and contrary to the optical microscope images, an order of efficiency could not be established among the different cleaners from the profilometric images. Nevertheless, on the 3D images water, KOH and Hostapon T® (Fig. 3b, d and e) showed major differences between the highest and the lowest points in comparison to the other cleaning solutions. This fact could be correlated with the major cleaning efficiency observed on the microscopic images. However, the cleaning effect produced by the cleaners was clearly different, what could not be recognized through the micro-pictures but on the 3D images, whereas rounded hills and valleys were visible in the topography after cleaning with Hostapon T® (Fig. 3e), sharper hills and valleys were achieved after the cleaning with water or KOH, cf. images b and d. Therefore, even though KOH solution and Hostapon T® produced the same visual effects and cleaning efficiency through the optical microscope, the topography features achieved after their cleaning were significantly different. In the case of water, micro-pictures and further quantitative roughness values were needed to evaluate its efficiency in comparison with KOH and Hostapon T®.

In the end, Brillianize® cleaning is worth mentioning because the surface topography showed in image f appears noticeably smoother in comparison with the other cleanings. A less-defined profile and the 'velvety' appearance suggested that the cleaner was not completely removed from the surface after the cleaning.

It can be pointed out that no additional scratches or further damages on the doll's surface were observed in the 3D images after the cleanings. In this case and probably due to the high roughness of the doll surface (arose from the manufacturing process or produced during the use of the doll), variations different from the removal of particles were not detected. This also means that any scratch produced during the cleaning process would have required a higher resolution to be detected, because of their small dimension, and therefore it had not significantly altered the morphology of the surface. Finally, topography's variation due to plasticizer removal or chemical reactions between the plasticized PVC and the cleaners was dismissed according to previous analyses (Morales & Egsgaard, 2011).

Additionally to the roughness values and the 3D images, line profiles were obtained from the profilometric analyses and evaluated before and after the cleanings (Fig. 4). According to the heterogeneous distribution of dirtiness along the doll surface observed in Fig. 3(a), the noncleaned surface showed a less homogeneous line profile (Fig. 4a) than the cleaned ones (Fig. 4b–f), where peaks and valleys were more regularly distributed along the mean line (centre line). Furthermore, differences in the peaks and valleys distribution were visible among the profiles after the cleanings. As in the 3D images (Fig. 3), the cleaning with KOH and Hostapon T® (Fig. 4d and e) produced less pronounced valleys than after the cleaning with water–ethanol (Fig. 4b and c), what was identified as more homogeneous cleaning effects. In the case of water, the valleys resulted noticeably less deep than in the other profiles, what indicated a less effective cleaning action. In addition, even though KOH and Hostapon T® produced similar cleaning effects through the microscopic images and the spectrocolorimetric values, the cleaning with KOH lead to higher peaks over the mean line than after the cleaning with Hostapon T® (Fig. 4d and e), what explained the different *Sq* values presented Table 1 for both cleaning solutions.

By contrast, the cleaning with the mixture water–ethanol produced a more homogeneous peaks/valleys distribution in the line profile in comparison with the water cleaning (Fig. 4c and b). This fact made clear the smaller *Sq* value obtained after the cleaning with water–ethanol (Table 1), because the 'neutralization' of heights and valleys along the profile diminished the total *Sq* value respect to the cleaning with water. At last, profile F (Brillianize® cleaning) presented significant differences with respect to the others. Despite the presence of some peaks and valleys, the roughness profile was closer to the centre line than in the other cases. This had a connection with the 3D image (Fig. 3f), where a less pronounced roughness was observed and identified with the residues left by the cleaners after the cleaning action.

Quantitative evaluation: cleaning efficiency

In combination with the traditional quantification by spectrocolorimetry used by other researchers as Kuisma *et al.*, 2005 and Gaspar *et al.*, 2003, the cleaning efficiency was established in this study by measuring the *Sq* parameter. This method of quantification was previously investigated in plasticized PVC cleaned by dry cleaning methods (Morales Muñoz, 2010).

As represented in Eq. (1), the *Sq* parameter computes the standard deviation for the amplitudes of the measured area surface (ISO 25178; De Chiffre *et al.*, 2000) and therefore, variations in the average roughness of the surface due to the removal of particles during the cleaning processes may be quantified and correlated to the cleaning efficiency. By contrast, damages caused by the cleaning could also vary the roughness parameters (Morales Muñoz, 2010), although this hypothesis has been dismissed because the cleaning was performed using wet cotton swabs softly rolled on the doll's surface. In addition, none of the scratches were detected on the

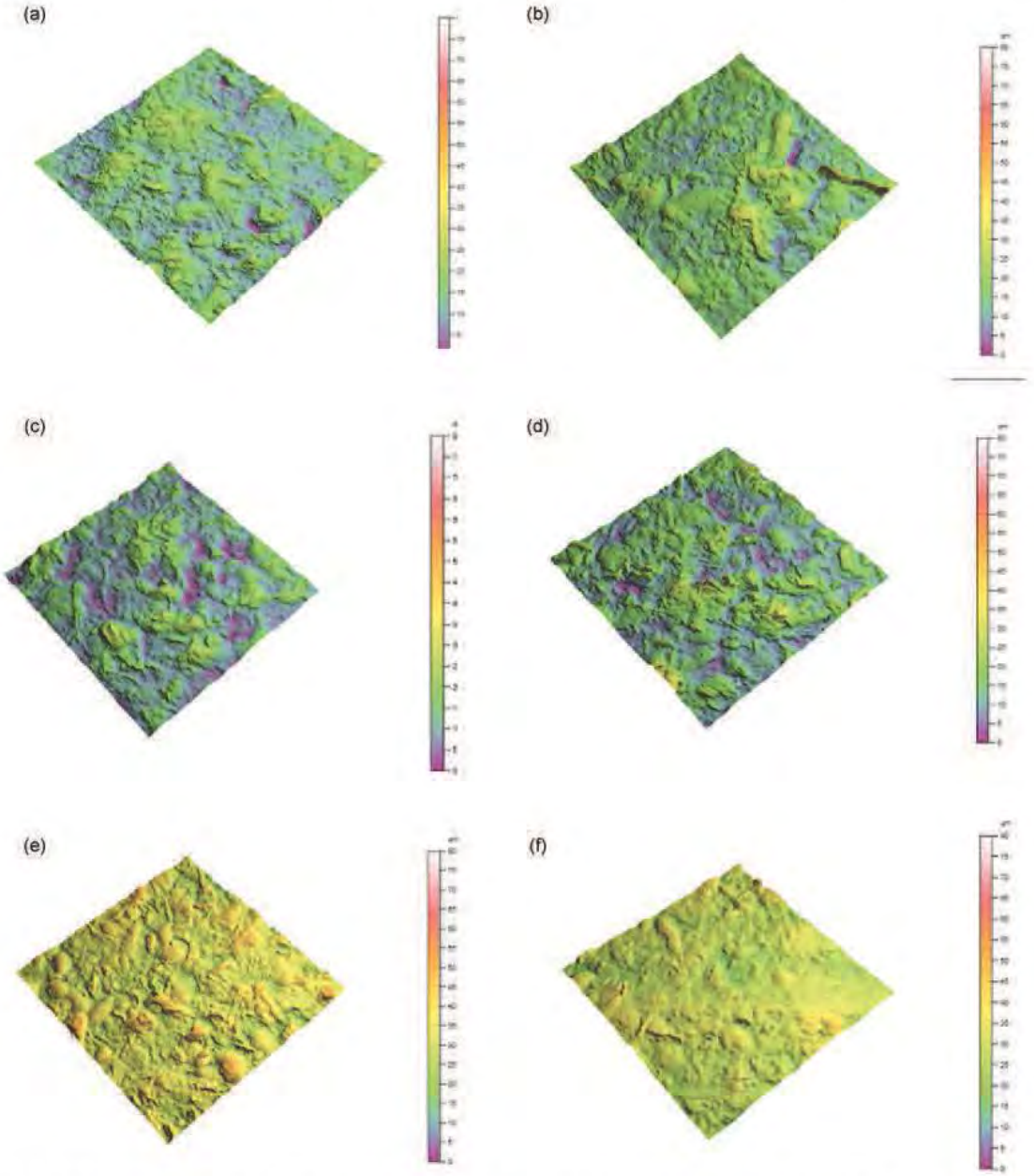

Fig. 3. Profilometric images from the doll surface before cleaning (a) and after cleaning with water (b), water–ethanol (1:1) (c), KOH 1M aq. (d), Hostapon T® 5% aq (e) and Brillianize® (f).

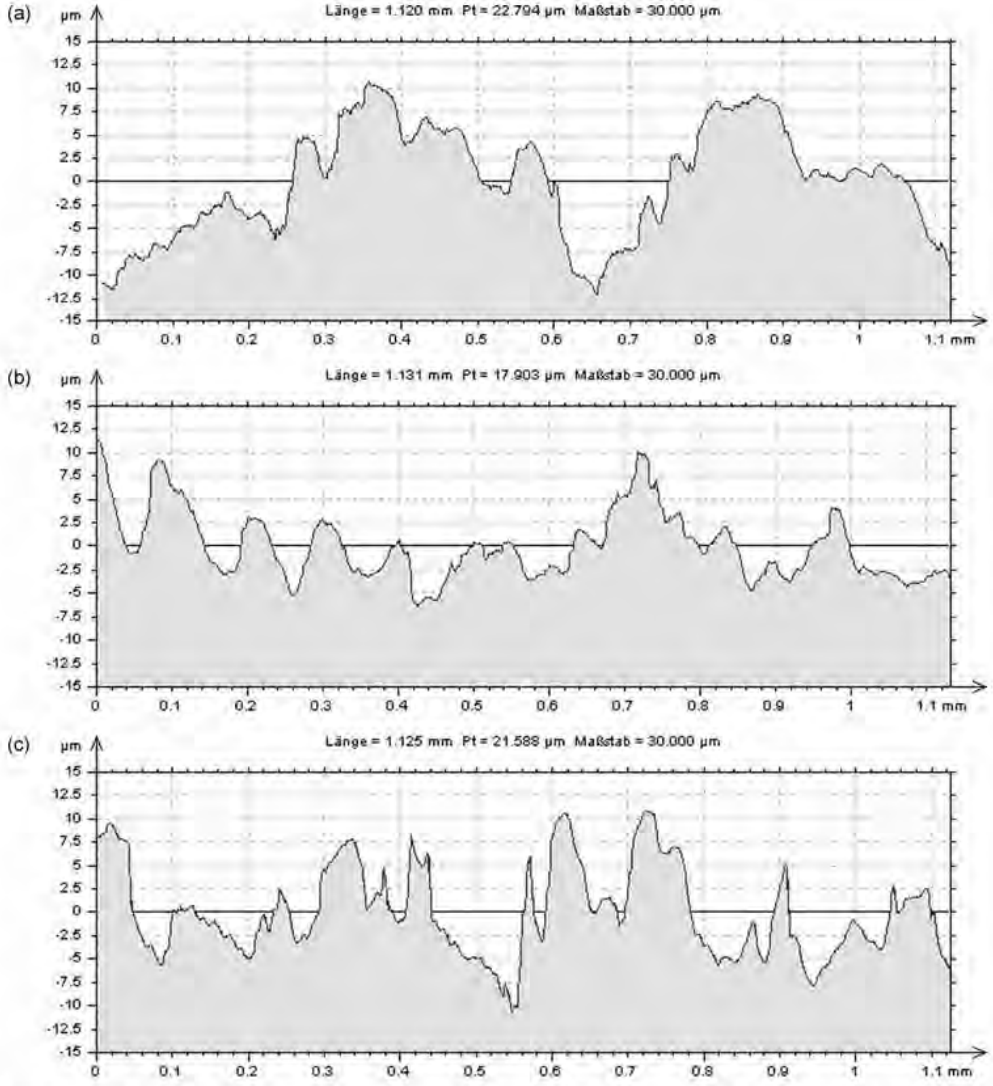

Fig. 4. Line profiles from the doll surface before any cleaning treatment (a) and after cleaning with water (b), water–ethanol (1:1) (c), KOH 1M aq. (d), Hostapon T® 5% (e) and Brillianize® (f).

3D images after the different cleanings. However, the variation of Sq with the cleaning must be carefully interpreted as further discussed in this work.

$$Sq = \sqrt{\frac{1}{A}\int\int_{A} z^2(x, y)\,dx\,dy}. \qquad (1)$$

The quantification by spectrocolorimetry is based in the measure of the lightness, which is represented by the L^* value or in the CIE $l^*a^*b^*$ space colour (Berger-Schunn, 1994). In the case presented in this study, the increase of L^* parameter has been interpreted as the removal of dirk dirtiness from the surface (Gaspar *et al.*, 2003), what corresponds to the observed on the micro-pictures. Therefore, the more the L^* value increase, the more effective the cleaning. However, when the surface and the particles deposited on the surface exhibit similar colour, or when the dirtiness is composed of colourless particles, colour variations cannot be detected and therefore

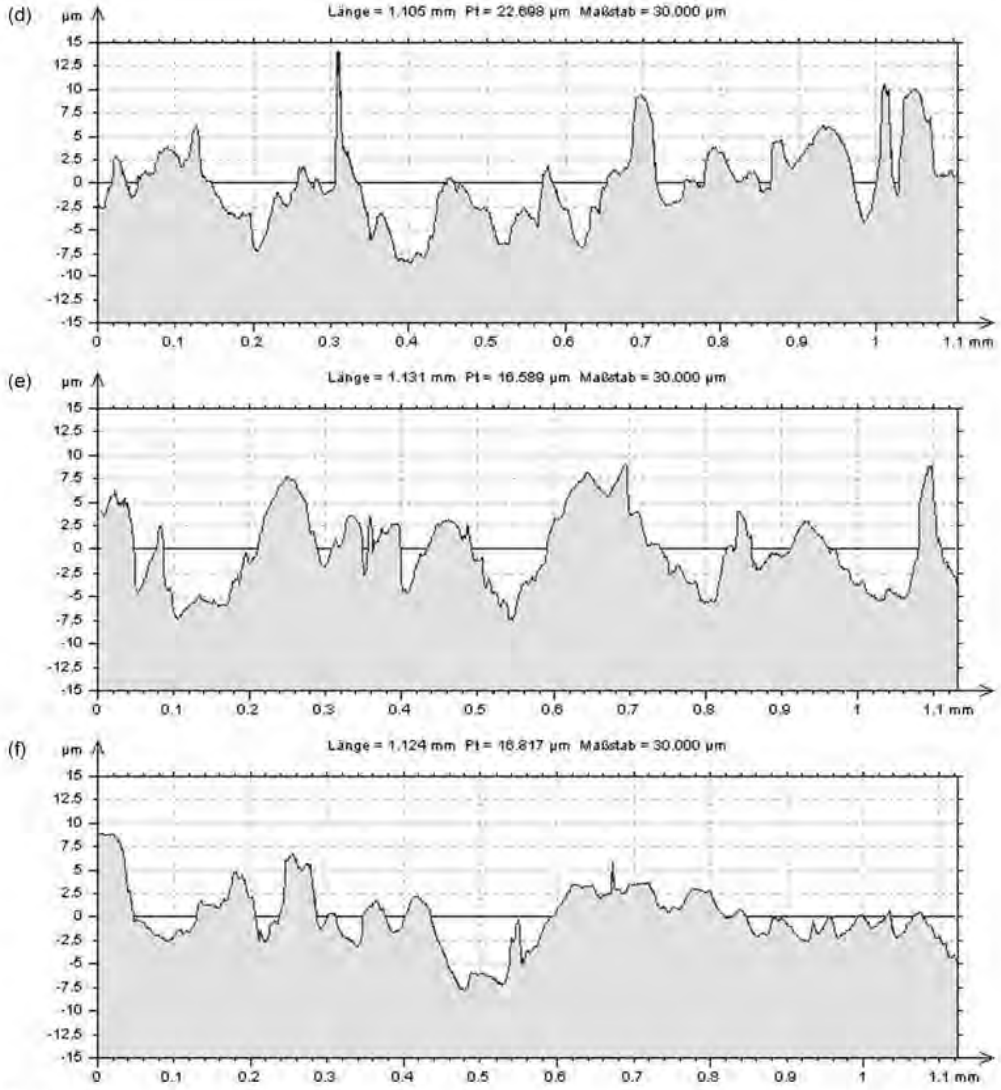

Fig. 4. Continued

spectrocolorimetric methods cannot be applied for assessment of the cleaning efficiency. An additional problem is the performance of the measurements with the spectrocolorimeter device, because this must be placed in perfect contact with the surface. This means that even though spectrocolorimetry is a nondestructive technique and does not require sampling from the object; its use is impeded by irregular morphologies or bumpy surfaces, which is the case in many 3D objects. Thus, the measurement of parameters independent of the colour variation, as roughness parameters, and the use of noncontact techniques, as noncontact profilometry, appears as an interesting alternative for the quantification of the cleaning efficiency.

To obtain statistical data, *Sq* and L^* were randomly measured on the doll surface (Fig. 5). Because of time–costs limitations, the initial *Sq* parameter was calculated from an average of nine measurements on the old doll's surface, whereas an average of four measurements was obtained for each cleaning system from its four replicate cleaned areas. The same number of measurements were performed for the

Table 1. *Sq* values and the standard errors of means (± SE) after the cleaning treatments.

Cleaning method	*Sq* (μm)
Before cleaning	4.3 ± 0.4
Water cleaning	4.7 ± 0.0
Water–ethanol cleaning	4.3 ± 0.2
KOH cleaning	5.7 ± 0.1
Hostapon T® cleaning	4.7 ± 0.1
Brillianize® cleaning	3.2 ± 0.1

Fig. 5. Doll head after cleaning with the cleaning solutions.

calculation of the L^* mean values before and after cleaning. *Sq* values were calculated by the profilometer according to ISO 25178 (Table 1). As it is shown in Table 1, the surface roughness changed after all the cleaning treatments, although significant differences were noticed among them. The *Sq* value clearly increased after the cleaning with water, Hostapon T® and KOH solution and diminished when Brillianize® was used. On the contrary, the cleaning with water–ethanol mixture lightly increased the *Sq* value, although it was accompanied by the highest standard error in the measurements.

The increase of *Sq* value was interpreted as the removal of particles from the surface, what led to a more irregular profile assumed to resemble the original surface. This assumption also agreed with the observed on the 3D and microscope images, where (although to different extents) particles of dirtiness were removed from the initial surface after all of the cleanings. From the *Sq* values, the most efficient cleaning solutions were KOH solution followed by Hostapon T® and water. The mixture water–ethanol seemed not to vary the *Sq* value, although the 3D pictures showed the achievement of a more determined rough surface after the cleaning as well as the removal of small particles strained between the hills and valleys. As previously mentioned, it has to be highlighted that *Sq* is a 'height parameter' that quantify the *z*-axis perpendicular to the surface (ISO 25178-2). For this reason, differences in the *x* and *y* directions (total *xy*-plane) must be additionally considered to completely understand the cleanings effect. Therefore, even though water did not show any difference in the total *Sq* value with regard to the noncleaned surface, the 3D images showed a clearly more cleaned surface. In the case of the cleaning with Brillianize®, the decrease of the *Sq* value was associated with the incomplete removal of the cleaner agent from the doll surface after the cleaning. This effect could be traced in the 3D image (Fig. 3f) where the surface topography appeared diffused. Therefore, the *Sq* value supported the previous hypothesis that the commercial cleaner was not completely removed from the surface after the cleaning.

In addition, even though the quantification of the cleaning efficiency may be established by means of the variation of the *Sq* parameter (Morales Muñoz, 2010), the roughness of the 'presupposed' original surface must be taken into consideration, because it strongly affects the interpretation of the results. For example, the doll surface before cleaning presented particles embedded on its surface. The removal of these particles with the cleaning revealed a more uneven surface (assumed closer to the 'original' one) and therefore a higher *Sq* value. On the contrary, when the initial surface is flat and smooth, its *Sq* value increases with the deposition of particles during the soiling process and newly decreases with the removal of these particles after the cleaning treatment. This fact was observed on the 3D images, when a soft and flat commercial plasticized PVC surface was cleaned and investigated in our previous experiments (Morales Muñoz, 2010). This plasticized PVC surface (Company VINK AS-Ref: 109200) turned rough after a natural soiling process and partially recovered its smoothness after 30 seconds cleaning with the commercial cloth PEL cloth®, commercialized for cleaning plastic surfaces in art conservation and composed of 70% polyester and 30% polyamide.

The L^* value represented in Table 2 showed a clear increase of the lightness after all the cleaning treatments in all the cases, which means that the dirtiness was removed from the surface in all the cases. However, major differences were observed among the cleaners. In agreement with the quantification by profilometry, the most effective cleanings corresponded to Hostapon T® and KOH solution, which presented the highest L^*, whereas water and water–ethanol mixture presented the lowest L^* value and therefore a relatively poor cleaning action. Contrary to the *Sq* values, Brillianize® showed a high L^* value, which apparently indicated a good efficiency. However, an in depth examination of the results concluded that the raise of L^* was not due to a better cleaning action but to the

Table 2. L^* values and the standard errors of means (± SE) after the cleaning treatments.

Cleaning method	L^*
Before cleaning	54.6 ± 0.6
Water cleaning	57.9 ± 0.1
Water–ethanol cleaning	57.9 ± 0.1
KOH cleaning	59.5 ± 0.5
Hostapon T® cleaning	59.8 ± 0.6
Brillianize® cleaning	58.9 ± 0.6

residual cleaners on the surface, what was supported by the fact that a whitish residue appeared on top of the samples when Brillianize® was air-dried and not wiped off from the surface. Also, distinctions between Hostapon T® and KOH solution or between water and water–ethanol mixture were not detected through L^*.

Conclusions

In summary, it can be stated that optical microscopy in combination with noncontact profilometry worked efficiently 'in tandem' for the assessment and quantification of the plasticized PVC doll cleaning, which corresponded to an old and dirty surface (pollutants, sweet, finger prints, etc). Not only the cleaning efficiency could be evaluated, but also the surface morphology achieved after the cleanings. With regard to the quantitative techniques used in this study, both spectroscolorimetry and profilometry provided complementary data, although more detailed information was obtained from the *Sq* values, which allowed to distinguish differences in effectiveness between cleaners that showed similar L^* values. This fact confirmed profilometry as an appropriate alternative to traditionally used spectroscolorimetry for quantification of cleaning treatments in conservation.

Among the solutions proposed for the plasticized PVC doll cleaning, significant differences were achieved regarding their effects and efficiency. From the optical microscope images and the *Sq* values, the cleaning with pure water and water–ethanol mixtures did not provided an efficient cleaning whereas the aqueous solutions KOH 1M and Hostapon T® resulted in being the most effective cleaners. However, even though the KOH solution provided the highest *Sq* value and thus a larger material removal, the 3D images showed a significant deep action, what may be considered as 'excessive cleaning' in conservation. On the contrary, the cleaning obtained by means of Hostapon T® was more homogeneous and less deep, what is a more suitable cleaning procedure in conservation. Finally, the 3D images, the *Sq* values and the L^* parameter indicated that the commercial product Brillianize® remained on the surface after the cleaning, what may produce changes in the object appearance and interfere with the correct preservation of the object.

Comparing the cleaning methods illustrated in the doll case with the dry cleaning methods already investigated in our former work (Morales Muñoz, 2010), it is relevant to mention that even in the case of the doll, cleaning methods based only on mechanical or electrostatic effects were not able to remove the organic dirtiness imbued with the plasticized PVC material. On the contrary, cleaning solutions were able to reach all the cavities on the rough doll surface and chemically remove the dirtiness. It can be concluded that the selection and succeed of dry or wet cleaning methods depend on the chemical, physical and topographical nature of both the artwork surface and the dirtiness on top, and therefore the cleaning methods must be selected according to all these factors.

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7.2. "Caso de Estudio: Limpieza de una muñeca Antigua de PVC con signos de degradación"

C. Morales Muñoz, H. Egsgaard

Proceedings from 11ª Jornada Conservación Arte Contemporáneo de Museo Reina Sofía, 83-92.

Caso de estudio: limpieza de una muñeca antigua de PVC con signos de degradación

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Dada la complejidad química de las obras de arte realizadas o compuestas por algún tipo de material plástico, su restauración y conservación es, en muchos casos, difícil para museos y conservadores, especialmente cuando la obra se encuentra en estado de degradación. A través de este caso de estudio, se ha planteado una metodología de limpieza destinada a objetos de arte realizados en plástico, y se ha testado en una muñeca antigua, fabricada con material de PVC y con signos evidentes de degradación.

INTRODUCCIÓN:
PLÁSTICOS EN ARTE Y SU CONSERVACIÓN

[1]
T. Van Oosten, Y. Shashoua y F. Waentig, 2002.

[2]
Y. Shashoua, *Conservation of Plastics. Material Science, degradation and preservation*, 2008.

[3]
H. Wilks, 1987.

Los materiales plásticos pueden encontrarse en museos y colecciones de arte [1], bien como objetos de la vida cotidiana que han adquirido un valor histórico-cultural o que de algún modo han sido incluidos en la categoría de obra de arte, o bien como materiales nuevos o reciclados utilizados para la creación artística [F. 01].

Por su particular complejidad química, los materiales plásticos presentan problemas de conservación diferentes a los que normalmente se encuentran en materiales tradicionales [2], los principales son: su rápido envejecimiento y degradación, (lo cual depende de la composición química, puesto que determinados tipos de plásticos envejecen o se deterioran más rápidamente que otros), y sus superficies particularmente electrostáticas y a veces pegajosas, que facilitan la adhesión de partículas y suciedad [F. 02].

La limpieza de cualquier objeto artístico es una práctica delicada [3] y por ello, ésta debe obedecer siempre a unos motivos concretos. Las principales causas que justifican una limpieza son: la preservación del objeto en sí mismo, ya que al eliminar la suciedad superficial evitamos que la superficie de

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F. 01. Página anterior izquierda.
Anders Krisár: *Cuirass*.
Colección particular. Realizado en silicona

F. 02. Página anterior derecha.
Oivind Nygaard: *Light Conductor*. SMK Museum.
Realizado en poliéster. En la parte inferior se muestra un detalle de la suciedad depositada en la superficie de la obra

F. 03
Cuadro sinóptico de metodología de limpieza para objetos de arte realizados en plástico

la obra pueda dañarse (por ejemplo mediante partículas abrasivas que rayen la superficie de la obra o productos de degradación que puedan dan lugar a reacciones secundarias que afecten a la superficie), así como garantizar el valor artístico del objeto y su correcta visualización, evitando que la posible suciedad depositada en la superficie distraiga la atención del observador y distorsione la percepción artística de la obra en su conjunto.

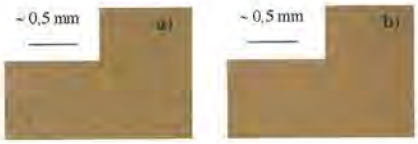
A la hora de describir la metodología de limpieza de un objeto de arte realizado en plástico, es necesario seguir una serie de pautas que garanticen un trabajo sistemático y efectivo. El cuadro sinóptico presentado en la [F. 03] recoge la metodología propuesta en este trabajo, que si bien ha sido aplicada a PVC plastificado, puede utilizarse para el estudio de limpieza de cualquier otro material plástico.

CASO DE ESTUDIO: LIMPIEZA DE UNA MUÑECA ANTIGUA DE PVC

El estudio de limpieza fue llevado a cabo en la cabeza de una muñeca danesa de los años 70 [F. 04], que había sido utilizada como juguete y que no había sido preservada bajo condiciones climáticas específicas para su conservación. La cabeza de la muñeca había sido fabricada de forma hueca y estaba compuesta de un plástico semirrígido.

F. 04
Muñeca danesa (años setenta)

F. 05
Micrografías correspondientes a muestras del exterior (a) e interior (b) de la superficie de la muñeca



OBJETIVOS

La realización de este caso de estudio tuvo como objetivos la obtención de tratamientos de limpieza específicos para obras de arte realizadas en PVC, así como la validación de la metodología general de limpieza propuesta [F. 03], para comprobar que las pautas establecidas fueran aplicables a cualquier objeto realizado en plástico.

CARACTERIZACIÓN DEL MATERIAL. IDENTIFICACIÓN DEL ESTADO DE CONSERVACIÓN Y DEGRADACIÓN DE LA SUPERFICIE

Muestras del exterior (con signos de suciedad) e interior de la muñeca (sin signos de suciedad) fueron observadas mediante microscopía óptica y profilometría de no-contacto, técnica que proporciona parámetros de rugosidad e imágenes 3D de los perfiles topográficos de las muestras analizadas [4].

[4] S. Fairbrass, 1999.

Las micrografías mostraron que la suciedad era evidente en la superficie de la muñeca y contrastaba con las muestras sin suciedad de zonas del interior de la muñeca [F. 05 a y b]. Mediante profilometría de no contacto se observó que la superficie presentaba cierto relieve y, por lo tanto, no se trataba de una superficie plástica homogénea y lisa. Las imágenes 3D mostraron que la suciedad no se componía de partículas depositadas en la superficie, sino que se encontraba embebida en el material plástico.

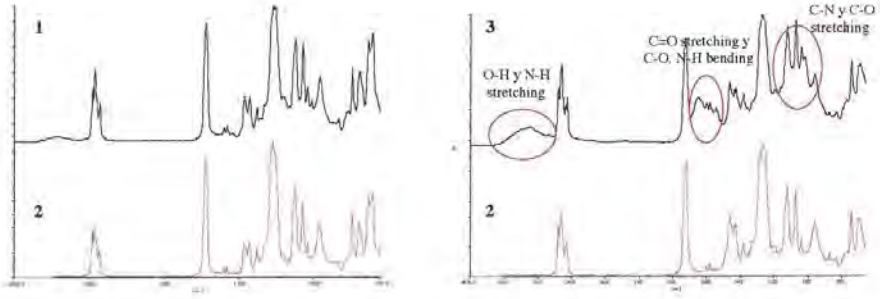
Las muestras fueron analizadas químicamente mediante espectroscopía ATR-FTIR [5] [F. 06], y así se pudo confirmar que el material de fabricación era PVC plastificado [F. 06 - 1, 2]. La suciedad superficial pudo ser identificada [6] [F. 06 - 3] con componentes orgánicos (lípidos, polisacáridos y otros) normalmente presentes en huellas dactilares, sudor, etc.

[5] J. L. Koenin, 1999.

[6] Derrick, Stulik y Landry, 1999.

El plastificante fue extraído y analizado mediante cromatografía de gases y espectroscopía de masas (CG-EM) [F. 07], utilizando dos tipos de columna cromatográfica: polar y apolar. En la columna polar fueron identificados di(2-etilhexil)ftalato(DEHP), así como 2-etilhexil ésteres de los ácidos grasos C12:0, C14:0, C16:0 y C18:0. En la columna cromatográfica apolar se detectaron los ácidos grasos C12:0, C14:0 (Mistírico), C16:0 (Palmítico) y C18:0 (Esteárico).

F. 06
ATR-FTIR espectros de:
1) superficie interior de la muñeca;
2) PVC plastificado (referencia);
3) superficie exterior de la muñeca
(los círculos en rojo corresponden a la suciedad superficial identificada con enlaces C=O, N-H y O-H de proteínas, lípidos, polisacáridos, etc.)



El di(2-etilhexil)ftalato(DEHP), correspondiente al plastificante, fue el aditivo mayoritario. El porcentaje de los ésteres C16:0 y C18:0 fue aproximadamente el 10-20 % del ftalato. La proporción de los ésteres C12:0 y C14:0 fue de un orden de magnitud inferior. La distribución de los ácidos grasos fue similar, aunque no idéntica, a la de los ésteres.

Dada la correlación entre de los ácidos grasos y los ésteres, una de las hipótesis que explicaría la presencia de ácidos grasos y ésteres en el PVC es que los ésteres fueran inicialmente utilizados como lubricantes internos en el PVC semi-rigido [7] y los ácidos provinieran de la hidrólisis de los mismos; proceso que no requiere reactivos adicionales (como agua) y que es a su vez catalizada por ácidos, lo que la convierte en auto-catalítica.

Sin embargo, también cabría suponer que tanto ácidos como ésteres fueron añadidos como lubricantes [8]. Esta hipótesis se basa en el hecho de que ambos productos fueron extraídos de muestras sin aparentes signos de degradación, y por tanto corresponderían a zonas del interior y del exterior de la muestras. Dado que los procesos de degradación comienzan en la superficie y posteriormente se extienden hacia el interior del material, deberían haberse encontrado ácidos y ésteres en la parte exterior de la muñeca y no solo en el interior, lo cual no fue visible en los ATR-FTIR espectros de la superficie de las muestras.

Por otro lado, se encontraron partículas blancas [F. 08] en gran parte de la superficie de la muñeca. Estos afloramientos han sido descritos en la bibliografía como una particular forma de degradación del PVC plastificado, que corresponde a lubricante migrado hacia la superficie e identificado como "ácido esteárico" [9]. Muestras de estos afloramientos fueron tomadas de la superficie y analizadas mediante espectroscopía ATR-FTIR y CG-EM.

El espectro infrarrojo correspondiente a las partículas blancas fue similar, pero no idéntico, al del ácido esteárico utilizado como referencia, al que fue comparado. Análisis mediante CG-EM confirmaron que se trataba de ácido esteárico y palmítico y no únicamente a ácido esteárico, como había sido referido en casos similares en la bibliografía [10]. El hecho de que únicamente los ácidos grasos C16:0 y C18:0 migraran a la superficie, puede deberse tanto a su mayor proporción en la composición del PVC en comparación a los ácidos C14:0 y C12:0, así como a su mayor facilidad de migración respecto a sus correspondientes 2-etilhexil ésteres.

[7] C.E. Wilkes, J.W. Summers, C.A. Daniels, 2005.

[8] *Ibidem.*

[9] Y. Shashoua, *op.cit.*

[10] *Ibidem.*

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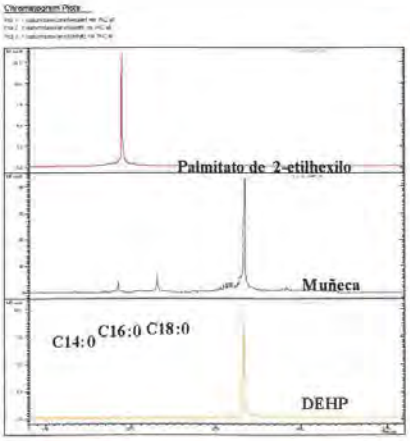
F. 07
Cromatograma: inferior, plastificante di (2-etilhexil) ftalato (DEHP) referencia; medio, plastificante extraído de la muñeca en el que se observan los picos correspondientes al plastificante y a los 2-etilhexil ésteres de los ácidos grasos C 14:0, C 16:0 y C 18:0; superior, 2-etilhexil éster de ácido graso referencia correspondiente al palmitato de etilhexilo (C 16:0)



F. 08
Detalle de afloramientos de partículas blancas en parte de la superficie de la muñeca

Respecto al plastificante di(2-etilhexil)ftalato, ningún producto resultante de su degradación fue identificado, lo que hizo suponer que el plastificante no había sufrido ninguna alteración y se encontraba en un adecuado estado de conservación.

PROPUESTA DE LIMPIEZA

La propuesta de limpieza se basó en agentes limpiadores en disolución [11], ya que la suciedad embebida en el plástico hacía inefectivos los agentes limpiadores en seco. Las disoluciones limpiadoras fueron propuestas de acuerdo a la eliminación de suciedad orgánica y productos de degradación presentes en la superficie de la muñeca e incluyeron: disoluciones acuosas y orgánicas, detergentes, productos comerciales específicos para plásticos, productos comerciales genéricos de limpieza de superficies, así como una disolución básica utilizada para la eliminación de suciedad orgánica pesada.

El principal riesgo que se consideró en la limpieza fue la extracción de plastificante y lubricantes [12]. Respecto del PVC polímero, los disolventes utilizados en las disoluciones limpiadoras fueron elegidos siguiendo la descripción de resistencia química de los laboratorios fabricantes de PVC, así como también se consideró el parámetro de solubilidad *Hildebrand parameter* del PVC [13] y de los disolventes limpiadores propuestos, de modo que fueran inocuos para el PVC. La extracción de plastificante fue previamente estudiada mediante espectroscopía ATR-FTIR. La absorbancia de la banda C=O del plastificante fue medida antes y después de la limpieza, por lo que se pudo determinar que no se producía una disminución significativa de la absorbancia tras la limpieza con las disoluciones propuestas.

[11] F. Huys y T.B. Van Oosten, 2005, pp. 335-342.

[12] D. Sale, 1988.

[13] Descrito por J. Burke, en *Solubility Parameters: Theory and Application. The Book and Paper Group. Annual Volume 3*, del American Institute for Conservation, 1984, pp. 13-58.

F. 09
Detalle de los ensayos de limpieza correspondientes a:
1) agua desmineralizada-etanol 1:1;
2) agua desmineralizada;
3) HostapoT 5% aq.;
4) Multiren;
5) Cleenmaster-Brillianize y
6) KOH 1M aq.

Las disoluciones limpiadoras utilizadas fueron: agua desmineralizada-etanol (1:1); agua desmineralizada (Millipore); HostaponT 5% en agua (detergente aniónico, sal sódica del ácido oleico metil taurida (64%); pH 7-8 (10g/l), solubilidad en agua 150g/l (20 C); Multiren (producto comercial genérico compuesto de iso-propanol, etanol y detergentes aniónicos); Cleenmaster-Brillianize (disolución acuosa comercial específica para la limpieza de plásticos) y KOH 1M en agua (pH ≥ 14). Las disoluciones limpiadoras fueron aplicadas mediante hisopos de algodón durante 10 segundos. HostaponT y KOH fueron aclarados con agua desmineralizada, mientras que las soluciones de agua y agua-etanol simplemente fueron secadas después de la limpieza. En el caso de los limpiadores Cleenmaster-Brillianize y Multiren, se siguieron las especificaciones comerciales indicadas, que recomendaban su eliminación mediante hisopos de algodón, secos y limpios.

El resultado del la limpieza pudo observarse visualmente tal y como se presenta en la [F. 09].

ANÁLISIS Y CUANTIFICACIÓN DE LA LIMPIEZA

Para la evaluación y cuantificación de la limpieza, se utilizaron varias técnicas. Primeramente, el examen visual determinó que las limpiezas realizadas mediante KOH 1 M y HostaponT resultaron más efectivas y homogéneas, mientras que el resto de las disoluciones limpiadoras produjeron limpiezas de menor eficacia.

Mediante espectroscopía ATR-FTIR, bandas correspondientes a la suciedad superficial fueron detectadas tras la limpieza realizada con todas las disoluciones limpiadoras, excepto con HostaponT y minoritariamente con KOH 1M.

Mediante profilometría de no contacto se determinó el parámetro de rugosidad Sq (raiz cuadrada media de la rugosidad de la superficie), utilizado para cuantificar la limpieza [14]. Puesto que el depósito de suciedad superficial generó con el tiempo una superficie homogénea en la muñeca, durante la limpieza, la eliminación de esta capa de suciedad permitió observar una superficie más rugosa, lo que dio lugar a un incremento del valor de Sq. Se observó que el mayor aumento del valor de Sq se produjo tras la limpieza con KOH y HostaponT. En el caso particular del producto Cleenmaster-Brillianize el valor Sq disminuyó, lo que indica que la superficie resultaba más homogénea tras la limpieza. Esta constatación llevó a la conclusión de que el producto permanecía en la superficie. El resto de las disoluciones limpiadores produjo incrementos de Sq menores que KOH y HostaponT, y por lo tanto, la eliminación de suciedad fue menor.

[14]
C. Morales Muñoz, 2010.

Dado el carácter especialmente básico de la disolución acuosa de KOH, se comprobó mediante CG/EM y ATR-FTIR espectroscopía que la disolución no hubiera afectado al plastificante superficial o lubricantes, ocasionando posibles reacciones tales como hidrólisis, etc. Puesto que el PVC es en sí

mismo resistente a disoluciones alcalinas concentradas, no se consideró la disolución alcalina de KOH como un posible riesgo para el polímero.

CONCLUSIONES

Mediante este trabajo se ha comprobado que la metodología propuesta es idónea para el estudio de limpieza de obras de arte realizadas en plástico. Asimismo, la aplicación de dicha metodología en el caso particular presentado: una muñeca antigua de PVC, ha permitido obtener métodos de limpieza efectivos y específicos para este tipo de obras.

También se ha comprobado que es absolutamente necesario definir métodos de limpieza particulares para cada tipo de plástico, ya que los productos genéricos pueden resultar no efectivos o incluso nocivos en ciertos modelos de elementos fabricados con este material.

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7.3. "Técnicas de examen para la limpieza en seco de superficies de obras de arte realizadas en plásticos"

J. Sanz-Landaluze, C. Morales Muñoz

Proceedings from 15ª Jornada Conservación Arte Contemporáneo de Museo Reina Sofía, 151-158.

Técnicas de examen para la limpieza en seco de superficies de obras de arte realizadas en plástico

JON SANZ LANDALUZE / CLARA MORALES MUÑOZ

Con el objeto de determinar con mayor exactitud los resultados de las limpiezas en seco sobre materiales plásticos y ofrecer alternativas de estudio apropiadas a las particularidades de obras de arte realizadas en dichos materiales, se propone la evaluación de distintas limpiezas utilizando diferentes técnicas de microscopía. Para ello, se han utilizado la microscopía óptica y profilometría de no-contacto como técnicas de examen de la limpieza de dos tipos de PVC (uno con plastificante y otro sin plastificante) mediante hisopos de algodón y 3 paños comerciales recomendados como limpiadores en seco de materiales plásticos. Los resultados recogidos muestran diferencias causadas tanto por la composición del material plástico como por la composición del agente limpiador en seco.

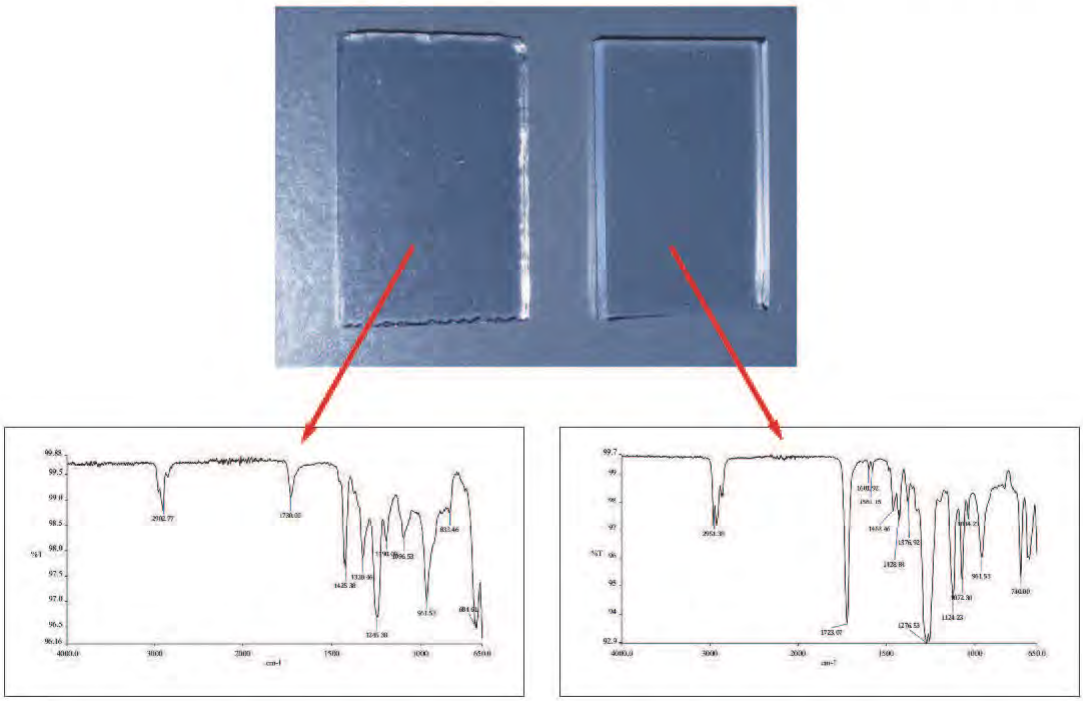
INTRODUCCIÓN

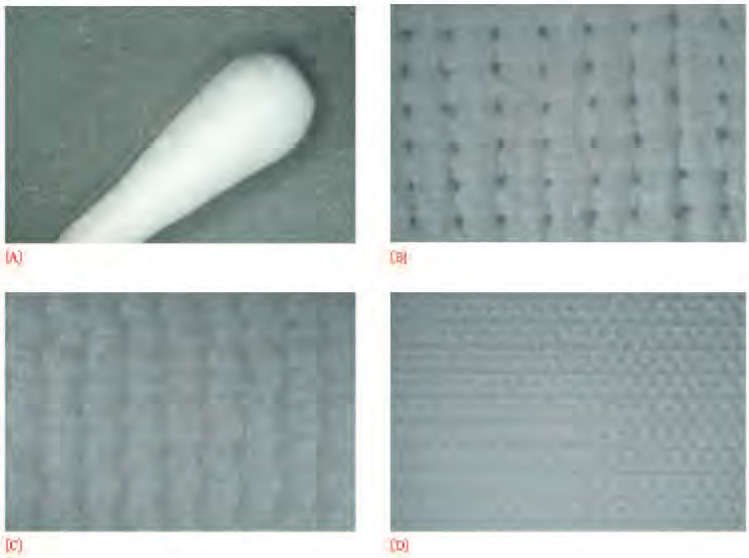
Para evaluar los resultados de limpiezas en seco sobre materiales plásticos y ofrecer alternativas de estudio apropiadas a las particularidades de obras de arte realizadas en plástico, se utilizaron diferentes técnicas de microscopía para observar alteraciones en muestras de PVC rígido y PVC plastificado que habían sido sometidas a limpiezas en seco. Las muestras de PVC rígido y PVC plastificado (fábrica danesa VINK) estaban en forma de lámina transparentes de 2 mm de espesor. El PVC no plastificado era rígido y fue proporcionado en piezas rectangulares. El PVC plastificado era una lámina flexible, que fue dividida en secciones pequeñas para la fase experimental [F. 01]. Ambos materiales fueron caracterizados mediante diferentes técnicas de examen tales como microscopía óptica y microscopía electrónica, y por medio de técnicas analíticas de cromatografía de gases-espectroscopia de masas y espectroscopia ATR-FTIR[1].

[1] Morales Muñoz, (2011).

[2] Ibídem.

Para la realización de las limpiezas en seco se propusieron agentes utilizados normalmente en conservación para la limpieza de materiales plásticos, seleccionándose hisopos de algodón y tres tipos de paños comerciales de diferente textura y composición especialmente recomendados para objetos fabricados en plástico: *Dust Bunny Cloth, PEL-Cloth™* y *PEL-Cloth™ Glass Cloth.* Todos los agentes de limpieza seleccionados fueron inicialmente examinados bajo el estereomicroscopio, realizándose micrografías a 0.512x aumentos [F. 02], y analizados químicamente mediante espectroscopia ATR-FTIR[2]. Se comprobó que los hisopos eran 100% algodón, mientras que los paños *PEL-Cloth™* y *PEL-Cloth™ Glass Cloth* resultaron ser una mezcla 70:30 de fibras de poliéster y





[F. 01]
Página anterior
Muestras correspondientes al PVC rígido (A) y PVC plastificado (B) utilizados y sus correspondientes espectros ATR FTIR.

[F. 02]
Hisopos de algodón (A), *Dust Bunny*, (B), *PEL-Cloth*™ (C) y *PEL-Cloth*™ *Glass Cloth* (D).

poliamida, así como el paño *Dust Bunny* estaba compuesto íntegramente por fibras de poliamida. Para el estudio de los resultados de las limpiezas se propuso el empleo de:

1) Microscopía óptica;

2) Profilometría de no contacto; y

3) Microscopía electrónica de barrido (SEM).

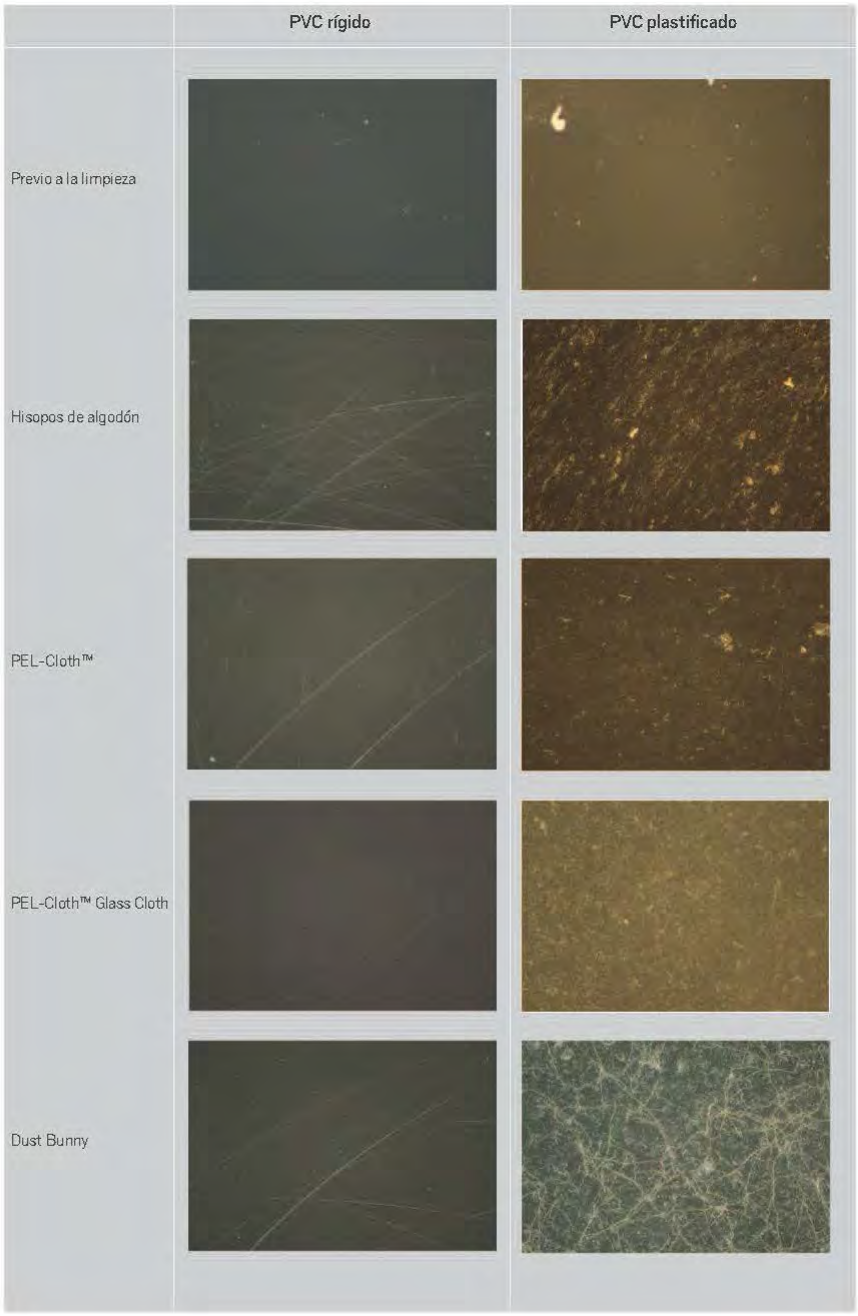
Si bien la microscopía óptica y electrónica han sido tradicionalmente utilizadas como técnicas de examen en el estudio de limpiezas en conservación de arte, la profilometría de no contacto ha supuesto una técnica novedosa en el estudio de limpieza de superficies de obras de arte compuestas en plástico, ofreciendo ventajas adicionales, tales como la obtención imágenes en 3D y el estudio topográfico de la superficie limpiada.

EXPERIMENTAL: MATERIALES Y MÉTODOS

Experimento 1

Se evaluaron limpiezas con los diferentes agentes en seco propuestos, las cuales fueron realizadas manualmente durante diez secuencias de 10 segundos (total de 100 segundos) en superficies de 1 cm^2 de las muestras de PVC plastificado y PVC rígido, con el fin de estudiar los resultados en ambos tipos de PVC y determinar posibles particularidades debidas a la composición del PVC y/o a los agentes de limpieza. Con el objeto de obtener resultados reproducibles, las limpiezas se realizaron en tres muestras diferentes de PVC plastificado y PVC rígido por cada agente limpiador. Los resultados de los agentes limpiadores en seco fueron observados mediante un microscopio Axiotech 100HD a 25x aumentos. Micrografías de varios puntos de la superficie del PVC rígido y plastificado fueron tomadas antes y después de las distintas limpiezas en las zonas acotadas [F. 03].

[F. 03]
Imágenes microscópicas de PVC rígido y PVC plastificado antes y después de limpiezas durante 100 segundos con los agentes limpiadores en seco (hisopos de algodón, *Dust Bunny cloth*, *PEL-Cloth™* y *PEL-Cloth™ Glass Cloth*).



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[F. 04]
Profilómetro de no contacto.

Experimento 2

Con el fin de contemplar la influencia del tiempo de ejecución del tratamiento en los resultados, se realizaron limpiezas de 10 segundos y 100 segundos en superficies de 1 cm^2 de muestras de PVC plastificado. Los efectos producidos se analizaron con un *profilometer Usurf Explorer*, proporcionado por la compañía alemana NanoFocus AG [F. 04], obteniendo imágenes topográficas en 3D de la superficie del PVC plastificado antes y después de limpiezas [F. 05].

RESULTADOS

La limpieza con hisopos de algodón produjo modificaciones de la superficie del PVC plastificado observadas como manchas blancas mediante microscopía óptica [F. 03] y como líneas en relieve a través de las imágenes profilométricas en 3D [F. 05]. Estas alteraciones fueron detectadas en las imágenes en 3D, tanto en las limpiezas de corta duración como en las de larga duración, por lo que el tiempo no tuvo un papel determinante. Sin embargo, cuando la limpieza fue realizada sobre PVC rígido, no aparecieron manchas blancas, sino rayado de la superficie. Análisis posteriores mediante espectroscopia ATR-FTIR confirmaron que las manchas blancas correspondían a la migración de plastificante en la superficie del PVC[3].

Se percibieron dichas manchas mediante microscopía óptica en las superficies del PVC plastificado, tras la limpieza con los agentes comerciales de poliamida-poliéster, si bien éstas no pudieron relacionarse con migración de plastificante[4], sino con restos de lo agentes limpiadores, ya que se observaron pequeñas partículas en las imágenes 3D obtenidas mediante profilometría de no contacto. Dicho efecto fue detectado con mayor claridad en las limpiezas de 100 segundos, por lo que el tiempo de intervención sí fue un factor influyente en los resultados.

La limpieza en seco mediante paños de poliamida-poliéster produjo efectos diversos en el PVC no plastificado tras su empleo durante 100 segundos: se observaron arañazos visibles únicamente cuando fue utilizado *PEL-Cloth™*, mientras que el paño *PEL-Cloth™ Glass Cloth* no produjo modificaciones de la superficie del PVC rígido.

[3] Morales Muñoz, (2010).

[4] Ibídem.

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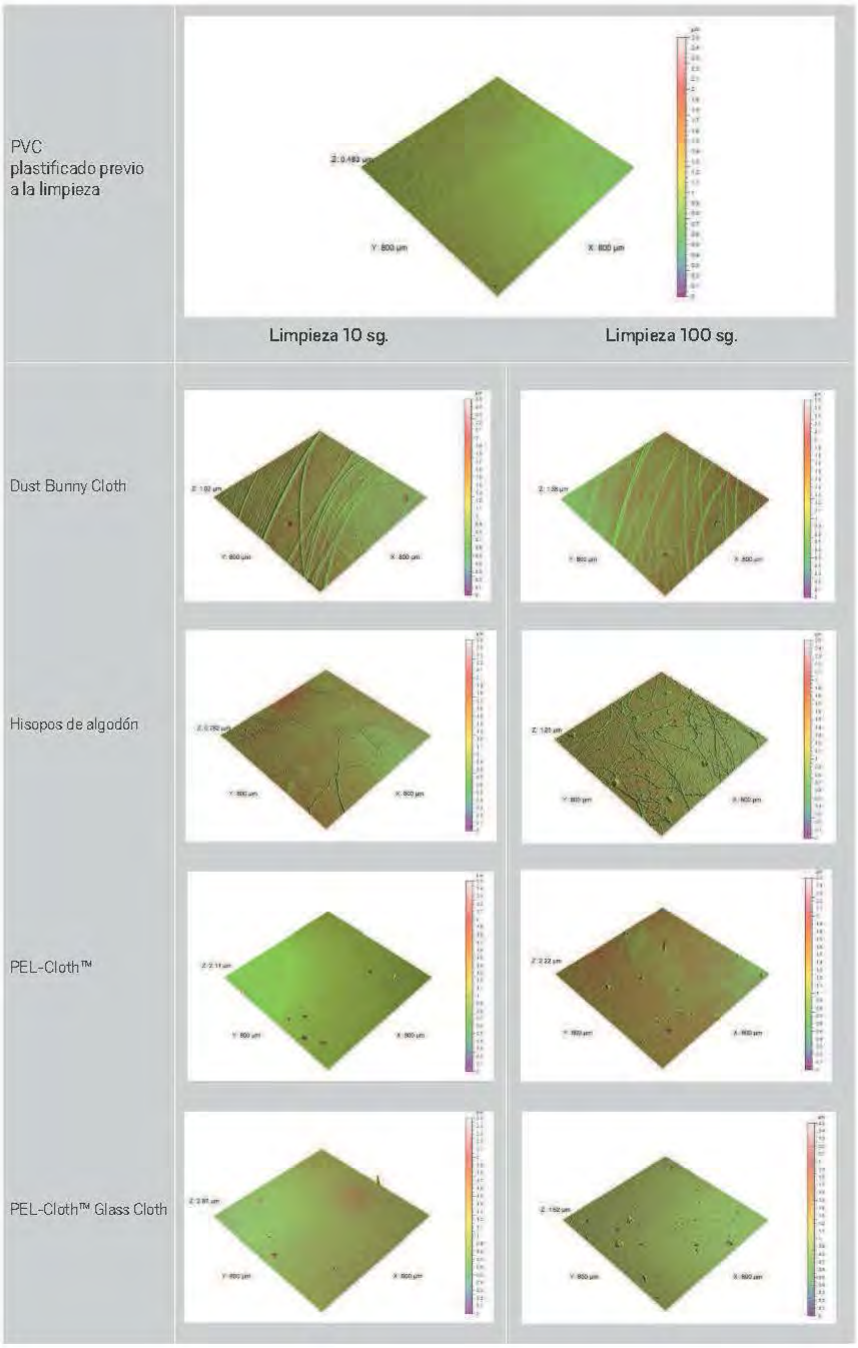
[F. 05]
Imágenes topográficas en 3D de PVC plastificado antes y después de limpiezas durante 10 segundos y 100 segundos con los agentes limpiadores en seco (hisopos de algodón, *Dust Bunny Cloth*, *PEL-Cloth™* y *PEL-Cloth™ Glass Cloth*).



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[F. 06]
Imágenes SEM de PVC plastificado: previo a la limpieza (A), después de limpiezas durante 100 segundos con *Dust Bunny Cloth* (B) y detalle de partículas, suciedad y fibras sobre PVC plastificado no sometido a ningún tratamiento de limpieza (C).

El empleo de paños de composición 100% poliamida produjo arañazos sobre la superficie de PVC no plastificado. Además, se observó un notable cambio de la superficie mediante microscopía óptica y profilometría en el PVC plastificado, tanto a tiempo de limpiezas cortas como de mayor duración. Exámenes posteriores mediante espectroscopia ATR-FTIR confirmaron la interacción del plastificante con las fibras de poliamida del agente en seco *Dust Bunny Cloth*[5]. A través de imágenes a alta resolución proporcionadas por el microscopio electrónico de barrido (SEM), pudo visualizarse que las fibras de poliamida no quedaban depositadas en la superficie, sino que parecían quedar inmersas en el polímero de PVC [F. 06], confirmando los resultados obtenidos mediante espectroscopia infrarroja ATR.

[5]
Ibídem.

CONCLUSIONES

A tenor de los resultados obtenidos mediante microscopía óptica y profilometría de no contacto, las limpiezas en seco han resultado en su mayor parte dañinas para las muestras de PVC y PVC plastificado utilizadas en esta investigación. Por tanto, esta técnica debe emplearse con cautela y teniendo en cuenta tanto la composición química del agente limpiador como la composición química del plástico que debe limpiarse, ya que ambos componentes han resultado determinantes en los efectos ocasionados. La técnica de examen en 3D, profilometría de no contacto, ha resultado adecuada y novedosa en el estudio de limpieza de superficies plásticas, proporcionando información complementaria a la obtenida mediante métodos tradicionales de examen como la microscopía óptica y la microscopía electrónica de barrido (SEM).

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CURRÍCULUM VÍTAE

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8. ARTIFICIAL PHOTO-AGEING

Cleaning methods have been commonly used for artworks cleaning. However, their use and effects on degraded plastics surfaces have not been deeply investigated. In order to provide a better understanding of cleaning methods on degraded plastics surfaces, plasticized PVC has been artificially degraded and used as sample material to test cleaning methods.

The main purposes targeted were:

a) Investigation of the degradation compounds formed after the photo-ageing of the plasticized PVC used as sample material;

b) Understanding of the degradation pathway and possible interpretation of the degradation mechanism;

c) Assessment of the degradation stages of the plasticized PVC material in relation with time.

Photo-degradation of plasticized PVC: a perspective for artworks cleaning

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PHOTO-DEGRADATION OF PLASTICIZED PVC: A PERSPECTIVE FOR ARTWORKS CLEANING.

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Abstract

Polyvinyl chloride (PVC) is actually one of the raw components of important collections in museums. Several reports inform about severe degradation problems in museum environments affecting both, the aesthetical aspect of the artworks and their integrity. The correct identification of the chemical components of the material and its degradation products is necessary to develop suitable cleaning methods in order to preserve them. The degradation of a plasticized commercial PVC by means of artificial photo-ageing has been assessed. The degradation of the PVC polymer and the phthalate ester plasticizers in the polymer has been investigated, finding several degradation products such as alkenes, phthalic anhydride, benzoates and alcohols. The influence of thermal and UV stabilizer in the material degradation has been also analysed. Physical and chemical changes have been monitored during four weeks in order to understand the extent of the material degradation over time. Eventually, a Norrish II mechanism has been identified for the formation of alcohols and phthalic acid during the ageing process.

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1- INTRODUCTION

Synthetic polymers form part of many objects of our cultural heritage (1) and their use is expected to increase in the future. Within collections, there are many plastics objects that show some level of degradation and are in need of cleaning (2). Since the aesthetical aspect is essential for the exhibition of the object, the cleaning of plastics supposes a serious concern for conservation community, who has become aware of the problematic related to these sensitive materials (1, 2, 3). Within the restoration process, cleaning is a delicate step that must be carefully assessed (4). In the case of degraded materials, the correct characterization of both the degradation products and the degradation pathways are essential for the selection of appropriate conservation treatments (5, 6, 7), Contrary to traditional work of arts, plastics' composition and degradation pathways are highly diverse, which add difficulties to their understanding from a conservation perspective. In many cases, the degradation of a plastic material yields a protective layer on the surface that avoids further degradation of the inner polymer core (8, 9). However, these degradation materials also attract pollutants and dust, increasing the degradation processes (10). In addition, the longevity of plastics objects also depends on their composition and additives (11), which has an influence on type and extend of degradation and ageing processes. Thus, suitable cleaning methods are demanded by conservators and restores in museums in order to preserve both the aesthetical aspect and the material of plastics objects. For this purpose, the correct identification of the chemical components of the material and its degradation products is necessary to determine which cleaning method should be applied in every stage of the ageing.

Among plastics, polyvinyl chloride (PVC) is not only one of the most used polymers in the world (12), but also reported to be suffering severe degradation problems in Museum environments (2). Furthermore, PVC is one of the most sensitive polymers towards UV radiation and it deteriorates within a few weeks when exposed to natural weathering (13). For that reason, artworks made of PVC must be protected from direct sunlight radiation. However, during the artwork´s lifetime, non-ideal conditions

most probably have affected the material. Additionally, recycled materials already exposed to levels of UV radiation may be part of the artwork itself. Furthermore, artworks are sometimes displayed in outdoor conditions, or as part of installations making use of strong illuminating sources, which may cause the deterioration of the material.

Photochemical reactions and photo-physical processes are produced when radiation is absorbed. Since UV radiation is more energetic that visible light, this is the major degradation factor for the polymers, which are in general transparent to radiations above 400 nm. Raw PVC polymer absorbs UV radiation below 190-200 nm (14), while the UV radiation component in sunlight starts at 290 nm and common windows glass absorbs over 90% of light below 300 nm. However, many products and defects formed during the processing of the plastic or plasticizers added to the PVC polymer to make it flexible, absorb UV wavelengths higher than 200 nm (15) and may be a "starting point" of the degradation of the PVC material. The carbonyl and aromatic groups present in phthalate ester plasticizers, for instance, absorb radiation of wavelengths higher than 290 nm, as well as conjugated double carbon bonds absorb radiation above 250 nm.

In order to contribute to the preservation of plasticized PVC objects in art collections, the present study is part of a series of investigations that have attempted to help understanding the cleaning processes of plasticized PVC in both non-degraded and degraded conditions. For this purpose, a commercial plasticized PVC material already used in previous investigations (16) was employed as testing material in the current research. The commercial plasticized PVC was exposed to artificial photo-ageing (13, 16, 17, 18) until visible degradation signs of the plasticized PVC surface were achieved. As a result of this research, a comprehensive model of the physical and chemical modifications of plasticized PVC samples could be achieved and a chemical mechanism explaining the formation of the main degradation products be proposed.

The degradation process on the surface was physically and chemically monitored by means of optical microscopy, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) (19, 20) and UV-Visible spectroscopy, while colour and gloss changes were assessed by means of spectrocolorimetry (21, 22) and gloss measurements. On the other hand, the photo-degradation products were analysed and quantified by means of gas chromatography and liquid chromatography coupled to mass spectrometry (GC-MS and LC-MS) (23).

2-MATERIALS AND METHODS

2.1. Reagents and reference compounds

All solvents (di-iso-propyl ether, ether, benzene, ethanol, cyclohexane, acetonitrile) were analytical grade or superior quality with a purity higher that 99,5% purchased from Merck (Darmstadt, Germany) or Fluka (Steinheim, Germany). Other reagents used: (di-isononyl phthalate (DINP), dioctyl adipate (DOA), 2-(2-Hydroxy-5-methylphenyl)benzotriazole, KOH, 2-Hydroxy-4-(octyloxy)benzophenone, 2-ethylhexyl mercaptoacetate, 1-nonanol, phthalic anhydride, benzoic anhydride, ammonium formate, formic acid), were also analytical grade or Pestipur from Sigma-Aldrich and Fluka (Steinheim, Germany). High-purity water with a resistivity of 18.0 MΩ·cm was obtained from Millipore (Bedford, MA, USA) ZMFQ 23004 Milli-Q water system.

The alcohols used in manufacturing of the plasticizers were recovered by Soxhlet extraction of the plasticizer (5 g PVC, ethanol, 90 min) followed by saponification (ethanol, 3.0 g KOH). After dilution with water (1:1) an extraction with ether:benzene (1:1) in the overall ratio 10:1 was carried out. The organic phase was dried and evaporated yielding a crude alcohol used directly for reference purposes and preparation of additional derivatives.

Several standards of different known concentrations were prepared by means of a standard solution 1:1000 of 1-nonanol and cyclo-hexane, and used for the quantification of the nonyl-alcohols. Phthalic anhydride was used to verify the formation of phthalic anhydride and preparation of the semi-esters. Nonyl benzoate was prepared by reacting equi-molar amounts of 1-nonanol and benzoic anhydride for 9h at 65ºC. The samples of the alcohol patrons, the phthalic anhydride and the nonyl benzoate were analyzed by GC/MS, following procedure described below.

2.2. Plasticized PVC Samples

The PVC used for this research was a nearly colourless plasticized PVC sheet of 2mm thickness supplied by the Danish company VINK (Product ref: 109200). The product was manufactured by the company Extruflex (France), (specialized in extruded PVC products), which provided a detailed datasheet describing various physical properties (Annex 1). However, no information was given regarding the specific composition of neither the plasticizers used nor the heat or UV stabilizers added.

2.3. Gas Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry was performed on a Varian 3400 gas chromatograph interfaced to a Saturn II ion trap mass spectrometer. 1 µL samples were injected manually using a micro syringe, and introduced in split mode (approximately 1:50) at a temperature of 250ºC. The temperature of the transfer line and the manifold of the mass spectrometer were 250ºC and 200ºC, respectively. The photo-degradation products were separated using a 0.32 mm i.d. x 30 m WCOT fused silica column coated with VF-23ms at a thickness of 0.25 µm. Separation of a wide range of products was achieved using a temperature program from 50ºC to 250ºC. Full mass spectra were recorded every 0.5s (mass range m/z 41- m/z 450). Photo-degradation products were identified using NIST/EPA/NIH Mass Spectral Library (NIST 08) and NIST Mass Spectral Search Program (Version 2.0f).

Plasticizers were extracted from PVC by Soxhlet extraction using di-*iso*-propyl ether for six hours and analysed by GC-MS, while alcohols used in the manufacturing of the

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plasticizers were recovered by Soxhlet extraction of the plasticizer with ethanol, followed by saponification at reflux. The nonanols were extracted with ether:benzene 1:1 after dilution with water. The organic phase was dried and evaporated yielding a crude alcohol and analyzed by GC-MS.

For the quantification of the nonanols (C9-OH) in the commercial PVC during the photo-ageing process, a sample of PVC of approximately 2.5 g from each stage (first, second, third and fourth week) was immersed in 25 mL of cyclohexane for 1h. The liquids were collected in separated flasks to which 500 µL of an internal standard solution (IS) was added, prepared by diluting 1,5 mg of benzyl alcohol in 100 mL of cyclohexane. The solvent in each flask was reduced by a rotary-evaporator to approximately 1 mL and eventually using a stream of N_2 to 0.2 mL and analyzed by GC-MS. The obtained peak areas (corresponding to Samples/IS) were interpolated in a calibration line, previously calculated by means of a standard solution of 0.1 mL of a reference nonanol (C9-OH) in 100 mL of cyclohexane.

2.4. Liquid Chromatrography –Mass Spectroscopy (LC-MS)

The Liquid Chromatography Mass Spectroscopy analyses were carried out on-line using a LCQ (Classic) MS^n system (Finnigan, San Jose, CA, USA) bundled with an ESI (electro-spray ionization) source and a complete TSP HPLC system (Thermo Separation Products Inc., San Jose, CA, USA). The HPLC system consisted of a P4000 gradient high-pressure pump, a SCM vacuum degasser, an AS3000 auto-sampler and a UV6000LP PDA-detector. The reverse phase chromatography was performed using a Purospher RP-18e (125 x 4 mm, 5µm) column (Merck, Germany). The mobile phase (0,3 ml/min) was a gradient constructed from 100 % water (I) and 90 % acetonitrile v/v containing ammonium formate (40 mM) and formic acid (20 mM) (II) as follows (time, % II): 0, 5 %; 5, 5%; 20,100 %; 35,100 %; 40, 5%; 45, 5%. The samples were transferred into acetonitrile and 20 uL was injected. The chromatographic separation was carried out at ambient temperature.

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The LCQ system was operated in the normal mass mode (typical 50-500 u) with a maximum ion injection time of 200 ms. Negative ions were analyzed only. Source parameters: spray voltage – 3.5 kV, heated capillary 200 °C, sheath gas flow rate 80 (arb. units) and aux. gas flow rate 10 (arb. units).

In addition samples were analyzed directly using the syringe-pump system. The semi-ester was dissolved (0.5 mg/mL) in a 40 % v/v acetonitrile containing ammonium formate (20 mM) and formic acid (10 mM).

2.5. Optical Microscopy

Photomicrographs at 25x magnifications were taken from the plasticized PVC surface before and after the ageing stages, with an optical microscope Axiotech 100HD.

2.6. ATR-FTIR Spectroscopy

Plasticized PVC surface was analysed by ATR-FTIR spectroscopy, which has an infrared penetration of around 2 microns. For the analysis it was used a Spectrum One Spectrometer (Perkin Elmer), before and after the artificial degradation process. The spectra were recorded in absorbance mode, in the 4000-550 cm^{-1} range, at resolution of 2 cm^{-1} and 20 scans. The surface of the samples was in contact with a Diamond/ZnSe crystal with a 45° angle of incidence. The spectra were analysed without smoothening the data or baseline correction.

2.7. Spectrocolorimetry

The parameters L*, a* and b*, of the colour system CIELAB, were randomly measured on ten points of the plasticized PVC surface samples, before and after every exposition time, using a Colorimeter Minolta CM 2600D equipped with Standard Illuminant D65, 10 degree observer and specular component included. Average of the ten measurements were used to estimate the differences in the lightness-darkness (+ΔL*, -ΔL*), redness-greenness (+Δa*,-Δa*) and the yellowness-blueness (+Δb*,-Δb*) of the surface during ageing.

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In addition, the CIELAB colour difference formula: $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, was used to analyse and quantify the total colour change of the plasticized PVC during the photo-ageing.

2.8. UV-Visible Spectroscopy

Non-degraded and degraded samples were analysed at room temperature with no treatment, by placing them in the sampler holder of an UV-visible Spectroscopy Ocean Optics USB4000 UV-visible spectrometer with a Toshiba TCD1304AP 3648-element linear CCD-array detector. Spectra were recorded and presented as absorbance $A = -\log 10T$.

2.9. Gloss Measurement

The reflected light from the plasticized PVC surface before and after every exposition time was randomly measured on ten points of the plasticized PVC surface samples with a Minolta Multi-Gloss 268 Glossmeter. Since the samples surface went from high gloss to low gloss during the ageing process, an illumination angle suitable for intermediate gloss surfaces measurements was settled, which corresponded to 60° (25).

2.10 Artificial ageing

In order to induce photo-ageing to the commercial plasticized PVC, accelerated ageing of samples of 13x6 cm^2 was conducted in an ATLAS CI 3000+ Weather-O-Meter, where the light source was a 1, 97 kW xenon lamp using Type S borosilicate inner and on outer filters. The lamp and filters selected were those that reproduced outdoor daylight conditions; the irradiance level, defined as radiant flux per unit area incident on a surface, was controlled by tracking the broadband 50w/m^2 (from 300 to 400nm) (24) and the temperature in the chamber was set to the minimum allowed, which was 46°C. The black standard temperature (defined as the highest temperature that specimens may reach, in order to control the temperature of the weathering device) (24) as 61±1°C and the relative humidity was 54±1%. The samples were artificially photo-aged on one side until the surface reached high levels

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of degradation, which corresponded to 672h of exposition (4 weeks). During the ageing, samples were taken out the chamber after 168h (1 week), 336h (2 weeks) and 504h (3 weeks) (Figure 1) for further investigation.

3. RESULTS

Micrographs showed slight differences between initial and 1 week (168h) photo-aged samples (Figure 2-A and B). However, multiple particles started being noticeable after 168 h of artificial ageing (Figure 2- C, D and E). The amount of particles increased from 1 week (168h) until 4 week (672h).

ATR-FTIR spectroscopy showed progressive peaks formation on the polymer surface during the artificial photo-ageing process. After the first stage of the photo-ageing process (168 hours), a peak at 1615 cm^{-1} started being detectable (Figure 3-b) .Two new peaks appeared after 336h at 3300 and 1688 cm^{-1} (Figure 3-c) and a broad band between 3000 and 3500 cm^{-1} was formed after 504 h (Figure 3-d and e). These results were supported by the ATR-FTIR analysis of the degradation products formed during the photo-ageing process and removed from the surface (Figure 4-a), confirming the formation of alcohols (O-H stretching bands at 3300-3200 cm^{-1}), keto compounds (C=O stretching vibration at 1685-1688 cm^{-1}) (26) and alkenes (C=C absorption at 1615 cm^{-1}) during the photo-ageing process (14, 27). In addition, aromatic derivatives (band at 1562 cm^{-1}) and a significant amount of plasticizer were detected (Figure 4-b).

Analysis by UV-vis-spectroscopy represented in Figure 5 showed the increase of the absorbance at 400-500 cm^{-1}, (visible region in the electromagnetic spectrum), indicating the generation of chromophore groups during the photo-ageing processes. It is significant the variation of the spectra between the second and the third week of photo ageing, due to the increase of the absorbance.

Colour changes monitored during the photo ageing process by spectrocolorimetry showed an increase of the CIELAB colour difference during all the photo-ageing processes (Figure 6 A), although variances were observed among the CIELAB parameters. Thus, L* parameter (lightness), increased during the first stage of the photo-ageing (168h-1week) while it decreased after the second week, continuing this patter until the end of the process (Figure 6-B). The decrease of the L* value on the graph indicates a loss of lightness during the photo-ageing. On the other hand, the a* parameter, (red +/green -) fluctuated on time and it was not possible to determinate any tendency in the Chroma (colourfulness) variation (Figure 6-C). The b* parameter (yellow +/blue -), turned from negative to positive during the photo-ageing process, what indicated the tendency to yellow of the samples during the ageing process (Figure 6-D). The measurement of gloss on the samples surface showed a continued loss of gloss during the photo-ageing process (Figure 7). However while a mild decrease occurred during the first week of ageing, a significant lessening was noticed after the second week of the photo-ageing process.

By means of GC-MS, degradation products like aliphatic compounds, phthalic derivatives and benzoates were initially identified (Figure 8). Further analysis revealed the presence of C9 alcohols (28) (Figure 9), benzoates (29) (Figure 10) and phthalic anhydride (30). The plasticizer was identified as a mixture of di-isononyl phthalate (DINP) 96.4 % (Figure 11-a), and dioctyl (2-ethyl hexyl) adipate (DOA) 3.6 % (Figure 11-b). The total concentration of plasticizers in the PVC sheet was approximately 35% as determined gravimetrically. In addition, the GC-MS analysis revealed the presence of the UV stabilizer 2-(2-Hydroxy-5-methylphenyl)benzotriazole (CAS 2440-22-4) (Figure 11-c) (31).

Analysis by GC-MS of the recovered alcohols gave a rather complex distribution of nonanols, which was characterized by a relatively large fraction of the n-nonanol and accompanied by two major components. Interestingly, the distributions of the recovered free alcohols from the plasticizer and an authentic DINP were found to be essentially identical, pointing to a common chemical source.

From the experimental results, an almost linear increase of C9 alcohols was observed along the ageing process (Figure 12), while benzoates' concentration decrease along the photo-ageing stages (Figure 13-A). On the other hand, Phthalic Anhydride increased during the ageing process, even though the linearity of their growth was not as clear as for the alcohols (Figure 13-B).

By means of LC-MS, the formation of iso-nonyl-monoester of phthalic acid in the photo-aged plasticized PVC sheets was determined based on cyclo-hexane extracts. The cyclo-hexane solvent was exchanged for acetonitrile prior to LC-MS analysis to make the injected sample comparable with the mobile phase system. In Figure 14-a a typical chromatogram is shown. The monoesters elute relatively late and the separation takes place in accordance with molecular weight (32). In addition, branching of the alkyl chain introduces a fine structure of the chromatographic peak.

4- DISCUSSION

Both the formation of alkenes and the increase of the b* parameter (yellowing) during the first week of the photo-ageing could be interpreted as signs of typical de-chlorination and subsequent formation of double carbon bonds in the PVC polymer (15), which led to a pronounced yellowing of the surface. However, according to the micro pictures and ATR-FTIR spectroscopy analysis, the rate of plasticized PVC degradation was slow during the first week of the photo-ageing process and noticeable increased after the second week, yielding alkenes from polymer dechlorination, alcohols and acid compounds from oxidation processes (9, 33). Also, the increase of the UV/Visible absorption during the third week of photo-ageing suggests a higher degree of dehydrochlorination and polyene formation after the first two weeks of ageing (14).

On the other hand, neither significant degradation nor migration of the plasticizer was noticed during the first stage of the photodegradation according to the gloss measurement and ATR-FTIR analysis. However, after the second week of photo-

ageing the surface experienced an important decrease of gloss produced by the accumulation of degradation products (alcohols and acid compounds) and plasticizer migrated to the surface. This is due to the loss of compatibility between the plasticizer and the PVC polymer during the degradation of the PVC (15). From the identification of the degradation products by means of the GC and LC, the mechanism of the degradation of the main plasticizer (DINP) could be recognized as a Norrish II reaction.

The Norrish II reaction is a common photo-chemical reaction observed with compounds possessing aromatic carbonyl groups (28) and resulting in the formation of olefins and phthalic acid monoalkyl esters (30). A Norrish II reaction is a photo-chemically induced intramolecular abstraction of a γ-hydrogen. The reaction may most reasonably be considered to involve a 1,4-diradical. This transient product is stabilized as the iso-nonyl-monoester of phthalic acid by elimination of nonane (C_9H_{18}) (28) (Figure 15-a and 16). However, this monoester is thermally and chemically rather labile and gives rise to iso-nonanol and the phthalic acid/anhydride system (Figure 15-b). To demonstrate this, the Norrish II primary product of DEHP was used as internal standard for quantitative analysis of the corresponding product of the di-isononylphthalate (Figure 17).

The UV spectra of the PVC sheets on the experiments were characterized by a strong absorption with a well defined cut-off at 380 nm (Figure 5). This could not be neither due to the phthalate plasticizer nor to the PVC polymer, but to an additive (34). The screening analyses in former works (31) revealed the presence of the ultraviolet stabilizer 2-(2-Hydroxy-5-methylphenyl)-benzotriazole, whose UV-visible spectrum was in good agreement with spectrum obtained of the sheets. This compound is indeed one of the most studied UV stabilizers, and the intramolecular hydrogen bonding apparently is the origin of the rapid radiationless deactivation facilitating its widely use as photo stabilizer (35).

Thus, the photo excited enol rearranged into an excited keto-form before relaxation to its ground state keto-form by rapid internal conversion followed by isomerization to the thermodynamically favored enol-form (36). An interesting aspect is how a photo stabilized plasticized polymer, e.g. the phthalate/PVC system may undergo photo-degradation (37). Apparently this process may take place as the result of intermolecular hydrogen bonding between the plasticizer and the stabilizer (38). In addition, the photo-aging of the PVC sheets lead to a broad absorption in the visible region 400 – 500 nm due to the polyenes formation.

Thus, it could be stated that even though the material suffered from degradation from the first stage of the photo-ageing, its resistance was quite high over the first week, due to the UV stabilizers which were chemically identified in the commercial polymer. From the second week onwards, the efficiency of the photo-ageing stabilizers highly decreased and both physical and chemical degradation signs increased until a noticeable colour change and degradation layer were clearly visible on the PVC samples. The polymer degradation yields chromophore double carbon bonds, which produce the yellowing of the material, while the plasticizer (DINP) degraded into C9 alcohols and phthalic anhydride through a Norrish II reaction.

4- CONCLUSIONS

In contrast to other investigations, the current work has addressed the photo-ageing of plasticized PVC as a result of the chemical composition of the material including not only the PVC polymer and plasticizers, but also UV-stabilizers added during the manufacturing of the material.

From a chemical point of view, the photolysis products formed in the case of phthalates were olefins, alcohols and phthalic acid anhydride. The phthalate plasticized PVC has been characterized by the decomposition of the phthalate and by the cleavage of C-Cl bonds and formation of carbonyl groups bound to the polymer moiety.

As a characteristic feature, the photodegradation of the phthalate/PVC system caused an increase in the optical absorption the UV/VIS. In particular, irradiation at 254 nm resulted in absorption that extended to rather long wavelengths. Thus, this process became autocatalytic in the sense that an initial very weak absorption may result in significant changes of the product.

From the conservation point of view, the knowledge of the degradation products formed during the ageing of the material provides conservators with valuable information to approach the cleaning of the material and a more specific cleaning method may be applied. For instance, the cleaning of nonanols or benzoates formed during photoageing will require cleaning solutions different from other compounds such as inorganic particles accumulated on the surface. In addition, the identification of the ageing stage may help understand the physical and chemical changes of the polymer, leading to different cleaning approaches may be decided. This means, that the cleaning treatments necessary when mild signs of degradation has occurred (small colours and gloss changes, for instance) will differ from those necessary when strong degradation occur, such as the formation of visible degradation layers on the material's surface. Furthermore, the understanding of the degradation pathway will affect the decision of a cleaning action. Thus, degradation signs of the PVC material, such as changes in colour due to the formation of polyene groups, cannot be removed by a cleaning action, while degradation products formed on the PVC layer may be removed by means of a suitable cleaning action. This can be considered as a key factor in the conservators' criteria regarding the preservation of the original material with no conflict with the preservation of the material itself, although whether or not to remove them is a theoretical discussion out of the scope of the present work.

5- ACKNOWLEDGEMENTS

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the MCA- Marie Curie Actions organization. Special thanks to Kim Pilkjær Simonsen for help with UV-Vis Spectroscopy (School of Conservation, Copenhagen, Denmark) and Bent Eshøj for assisting with the artificial photo-ageing experiments (School of Conservation, Copenhagen, Denmark). ATR-FTIR spectroscopy analyses, Optical examination, artificial photo-ageing as well as colour and gloss measurements were performed at the School of Conservation, Copenhagen (Denmark). GC-MS and LC-MS analyses were performed at Riso-DTU laboratory (Technical University of Denmark).

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Figure 1. Commercial Plasticized PVC samples before the photo-ageing treatment (left) and after 168, 336, 504 and 672 hours (right) of artificial photo ageing

Figure 2. Optical micrographs of: fresh plasticized PVC (A), and after 168 h (B), 336 h (C) 504 h (D) and 672 h photo-ageing (E)

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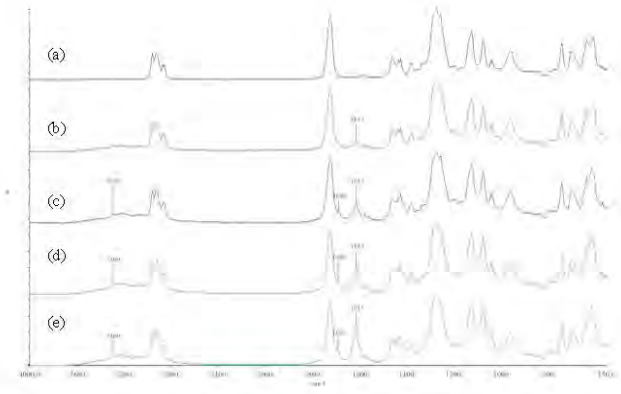

Figure 3. Commercial plasticized PVC before (a) and after: 168 h (b), 336 h (c), 504 h (d) and 672 h photo ageing (e)

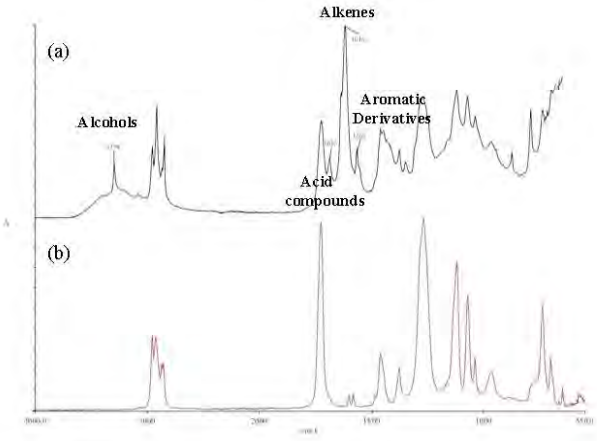

Figure 4. ATR-FTIR spectra of the degradation products mechanically removed from the surface of a 672h photo-aged commercial plasticized PVC (a) and plasticizer extracted from untreated commercial plasticized PVC (b).

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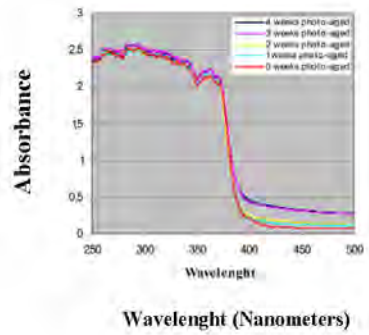

Figure 5. UV absorption spectra from the plasticized PVC surface before and during the photo-ageing process: 1 week (168h); 2 weeks (336h); 3 weeks (504h) and 4 weeks (672h)

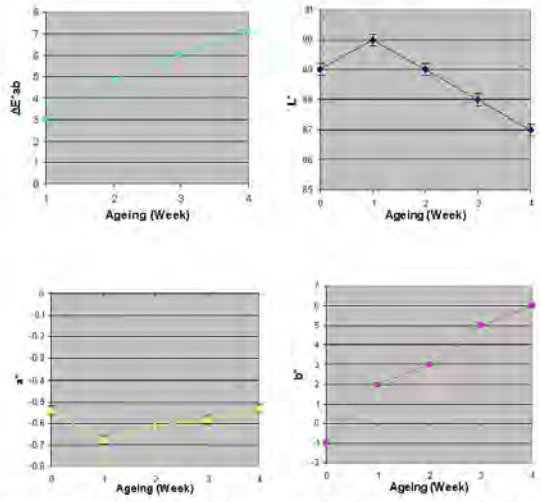

Figure 6. CIELAB A) colour difference of the plasticized PVC surface B) parameter L* of the plasticized PVC surface, C) parameter a* D) parameter b* during the photo-ageing process

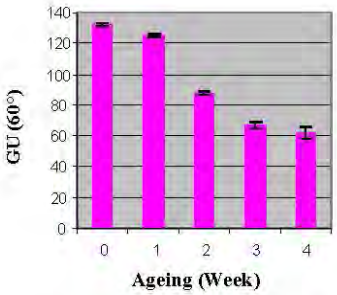

Figure 7. Gloss measurements and standard errors of means (±SE) before and during the photo-ageing process: 1 week (168h); 2 weeks (336h); 3 weeks (504h) and 4 weeks (672h).

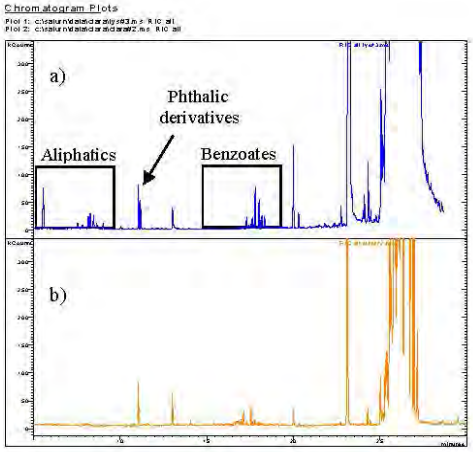

Figure 8. Total Ion Chromatograms of: (a) photolysis products isolated from plasticized PVC after artificial photo-ageing and (b) plasticizer extracted from commercial plasticized PVC

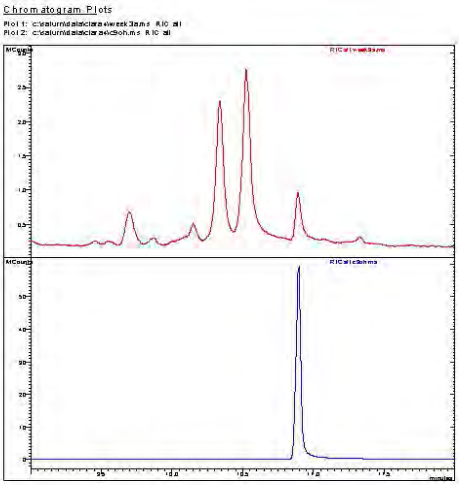

Figure 9. Extracted Ion Chromatogram of C9 alcohols isolated from (a) commercial plasticized PVC and (b) reference .

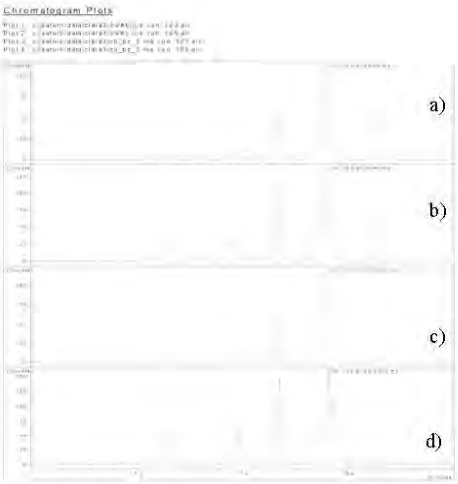

Figure 10. Ion 123 m/z and Ion 105 m/z mass spectra for benzoates isolated from commercial plasticized PVC (a, c) and synthesized in our lab (b, d)

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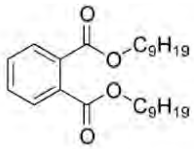
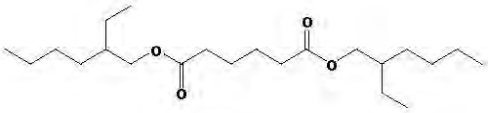
a)



b)



c)

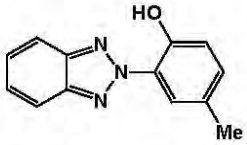


Figure 11. a) di-isononyl phthalate (DINP) 96.4 %, b) dioctyl (2-ethyl hexyl) adipate (DOA) and c) UV stabilizer 2-(2-hydroxy-5-methylphenyl)-benzotriazole.

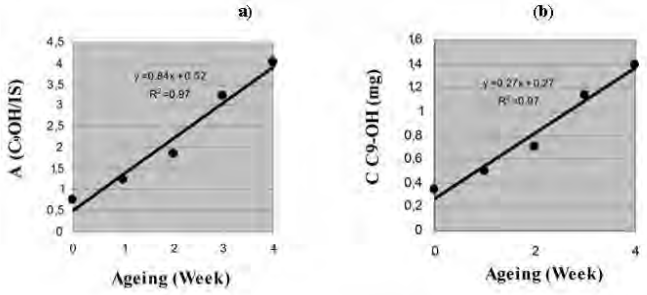


Figure 12. a) peak chromatogram ratio C9OH/IS during ageing and b) quantification (mg) of C9OH during the photo-ageing

24

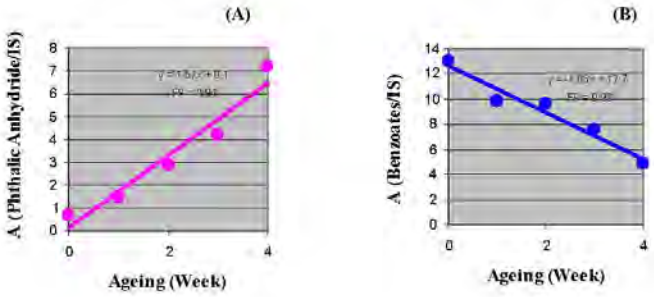


Figure 13. Peak chromatogram ratio Phthalic Anhydride/IS (A) and peak chromatogram ratio Benzoates/IS (B) during photo-ageing

25

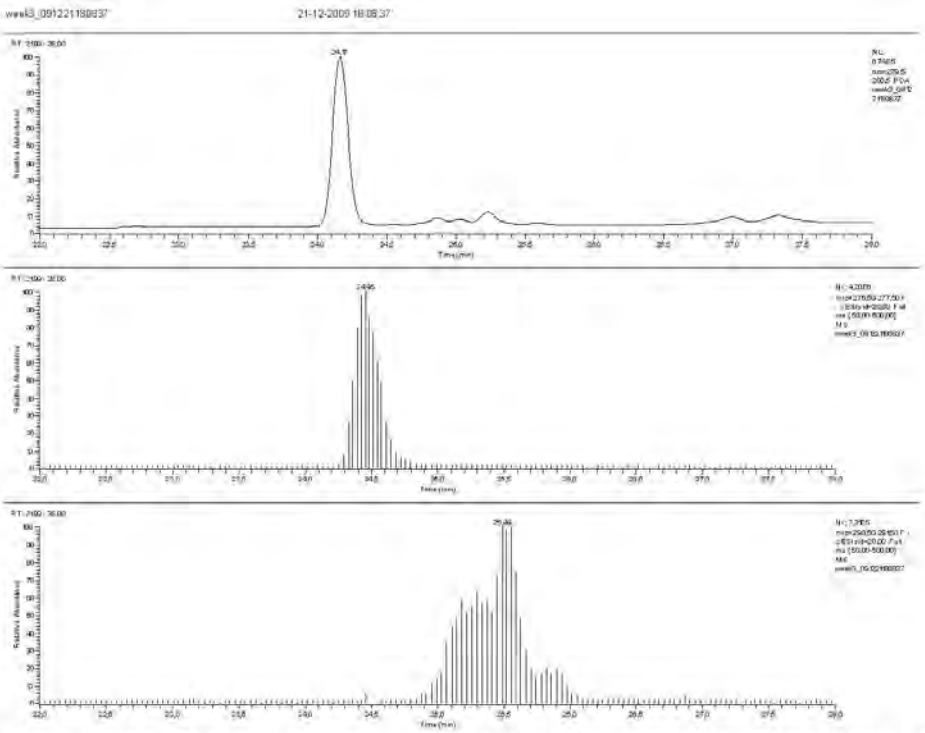


Figure 14: LC-MS in negative ion mode illustrating the separation of semi-esters of pthalic acid: a) UV trace (280 mm) (b) DEHP monoester (m/z 277) and c) isononyl species at m/z 291 (valid for all isomers).

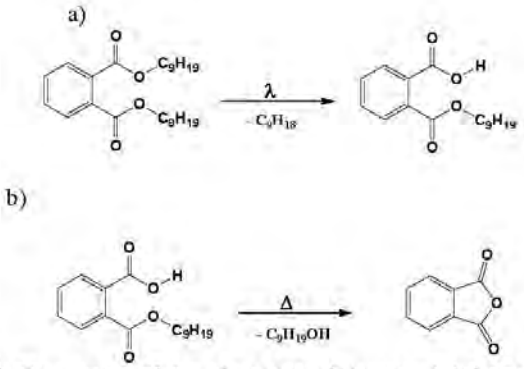


Figure 15. Norrish II reaction of the plasticizer di-isononylphthalate to form iso-nonyl-monoester by elimination of C_9H_{18} (a) and subsequent decomposition of the monoester into iso-nonanol and the phthalic acid anhydride system (b).

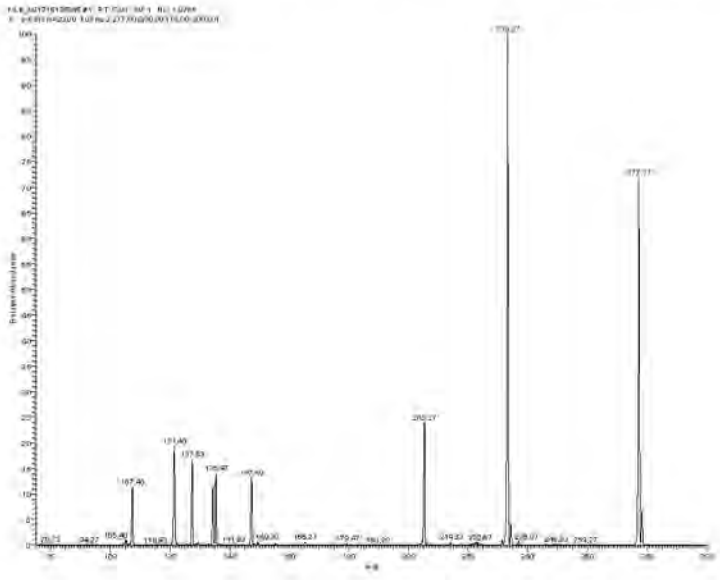


Figure 16. Collision activation of the anion phthalic acid 2-ethylhexylsemiester where m/z 277 is the parent anion, m/z 233 and 205 are due to the consecutive loss of CO_2 and CO.

27

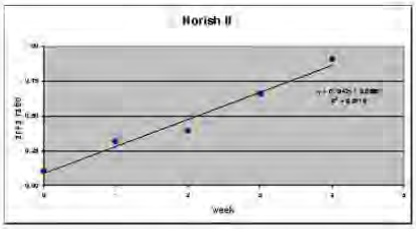


Figure 17. Quantitative analysis of the di-isononyl phthalate product formed by Norrish II reaction

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ANNEX 1: EXTRUFLEX PVC Technical Specifications

Values

PROPERTY	Standard	Units	Standard	Reinforced	Polar	Super Polar	Anti-Insect	Anti-static	High fire retardant	High UV resistant	Hard Neutral	Colored Opaque or Transp.	Screenflex (Welding)
Light transmittance	ASTM D 1003	%	85	85	85	85	< 80	85	85	80	85	0 to 80	≤ 13
Shore A hardness	EN ISO 868	Sh A	80	80	65	62	80	80	80	80	85	65 to 85	80
Tearing resistance	DIN 53515	N/mm	50	80	28	25	50	50	65	50	65	28 to 65	55
Tensile strength at break	ASTM D 638 EN ISO 527	N/mm²	16	16	12	10	16	16	20	16	20	12 to 20	18
Elongation at break		%	340	340	390	420	340	340	280	340	280	280 to 390	300
Residual elong. (after break)		%	68	60	76	80	68	68	60	68	60	60 to 76	62
Thermal conductivity	ASTM C 177	W/m.K	0,16	0,16	0,16	0,16	0,16	0,16	0,16	0,16	0,16	0,16	0,16
Cold bend brittle temp.	ISO 8570	°C	-35	-35	-40	-65	-35	-35	-20	-35	-20	-20 to -40	-25
Min. usage temp.	EN 1876	°C	-15	-15	-25	-60	-15	-15	0	-15	0	-15 to -25	-15
Max. usage temp.		°C	+50	+50	+30	+15	+50	+50	+50	+50	+50	+30 to +50	+50
Vicat softening temp.	EN ISO 306	°C	50	50	48	46	50	50	50	50	50	48 to 50	50
Specific heat capacity	ISO 11357	kJ/kg.K	1,6	1,6	1,6	1,6	1,6	1,6	1,6	1,6	1,6	1,6	1,6
Sound reduction	DIN 52210	dB	>35	>35	>35	>35	>35	>35	>35	>35	>35	>35	>35
Fire retardance	NF P 92-507 AS/NZS 3837 DIN 4102	Grade	Grp4 B2	Grp4 B2	-	-	Grp4 B2	Grp4 B2	M2 Grp 3	Grp4 B2	Grp4 B2	- / Grp4 - / B2	EN 1598
UV/IR filter	EN 1598	Filter	-	-	-	-	-	-	-	-	-	-	EN 1598
UV resistance	ISO4892	-	Yes	Yes	Yes	Yes	Yes	Yes	Yes	High	Yes	Yes	High
Charge buildup	IEC 61087	Sparks	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes
Surface resistivity	IEC 60093	Ω/□	4.10^{13}	4.10^{13}	4.10^{13}	4.10^{13}	4.10^{13}	2.10^{12}	4.10^{13}	4.10^{13}	4.10^{13}	4.10^{13}	4.10^{13}
Water absorption	EN ISO 62	%	-0,2	-0,2	-0,2	-0,2	-0,2	1 to 1,6	-0,2	-0,2	-0,2	-0,2	-0,2
Anti-insect	-	-	No	No	No	No	Yes	No	No	No	No	No	No
Density	ASTM D 792	g/cm³	1,22	1,23	1,18	1,18	1,22	1,22	1,33	1,22	1,29	1,2 to 1,5	1,2 to 1,3

The data contained in this technical specification is given for information only and is based on our current knowledge of the products concerned.
This information given to our customer in good faith to inform him and to help him in his search, does not constitute any formal or implicit guarantees as to its use.

Description

PROPERTY	Standard	Description
Light transmittance	ASTM D 1003	Visible light quantity transmitted through the material.
Shore A hardness	EN ISO 868	Index based on a flat indenter's penetration depth. Scale from 0 (Soft) to 100 (Hard).
Tearing resistance	DIN 53515	Minimum tensile stress required to tear a pre-slit sample.
Tensile strength at break	ASTM D 638 EN ISO 527	Maximum tensile stress that a material can be subjected to before break.
Elongation at break		Elongation of the specimen at the break point under tensile stress.
Residual elong. (after break)		Permanent elongation of the specimen measured after rupture in a tensile test.
Thermal conductivity	ASTM C 177	Ability to conduct heat. The Lower it is, the more insulation.
Cold bend brittle temp.	ISO 8570	Temperature at which the specimen break under torsion stress. Brittle point (CLASH & BERG).
Min. usage temp.	EN 1876	Temperature range where material keep its mechanical properties (flexibility).
Max. usage temp.		
Vicat softening temp.	EN ISO 306	Temperature at which the specimen is penetrated to a depth of 1 mm by a 1 kg flat indenter of 1 sq. mm.
Specific heat capacity	ISO 11357	Heat energy required to increase the temperature of one kilogram of the material by one degree Celsius.
Sound reduction	DIN 52210	Average sound level (freq. 0,1 to 3,2 kHz) decreased by a 1,76 sq.m. and 5 mm thick PVC curtain.
Fire retardance	NF P 92-507 AS/NZS 3837 DIN 4102	Standard classifications of material self-extinguishing and resistance to combustion.
UV/IR filter	EN 1598	Ability to filter welding rays allowing the use of this material as a welding protection screen.
UV resistance	ISO4892	Ability to resist to UV (Sun, welding arc).
Charge buildup	IEC 61087	Earthed sample is rubbed with cotton, acrylic and nylon rubbers. At electrode approach, spark appears or doesn't.
Surface resistivity	IEC 60093	Material surface electric resistivity measured with a 500 V direct voltage.
Water absorption	EN ISO 62	Material mass variation after exposure to humid conditions. (<0 if released / >0 if absorbed)
Anti-insect	-	Special ability to keep insects away.(Food processing plants, tropical regions)
Density	ASTM D 792	Mass per unit volume.

The data contained in this technical specification is given for information only and is based on our current knowledge of the products concerned.
This information given to our customer in good faith to inform him and to help him in his search, does not constitute any formal or implicit guarantees as to its use.

9. INTEGRAL DISSCUSION

9.1 Factors affecting the cleaning of PVC

As exposed in publications collected on Chapters 5, 6, 7 and 8, it could be proven that the results of the cleaning of PVC materials depend on the following factors: a) cleaning agents and PVC composition b) the topography of the surface, c) chemical nature of dirt and degradation products.

9.1.1 Cleaning agents and PVC composition

Chemical/physical modification of the commercial PVC sheet or residues from the cleaning agent after a cleaning treatment were not detected when water, Hostapon T 5% aq. solution, KOH 1% M or the commercial product Multiren were used. However, residues from the detergent solution Dehypon LS45 5% aq. got attached to the plasticized PVC surface, due to the lower solubility of this detergent in water (Chapter 6). In the case of the commercial product Brillianize-Kleenmaster, residues were not detected when used on the flat-sheet plasticized PVC (Chapter 6). However, residues of this commercial cleaner were visible by means of the 3D images obtained by profilometry when tried on the plasticized PVC doll (Chapter 7.1). The most probably cause here was the different topography of the PVC surfaces. Unlike the smooth and flat commercial PVC, the doll was rough and uneven, which made the removal of the cleaner more difficult. The latter tended to fill the space between valleys and hills in the topographical profile.

The ATR-FTIR spectrum of the plasticized PVC showed significant changes after cleaning with pure organic solvents such as ethanol, propanol or heptane, due to plasticizer extraction during the cleaning (Chapter 6paper 6.1). However, organic solvents mixed with water in proportions that did not cause any chemical or physical

alteration of the plasticized PVC were achieved by means of the "Plasticizer Index" defined in Chapter 6. As a result, a 2:1 water-ethanol mixture was found to be suitable for the cleaning of commercial plasticized PVC.

Dry cleaning methods led to physical alteration of the plasticized PVC when cloth composed of 100% nylon fibers were used (Chapters 5 and 7.3). These alterations were visible by optical microscopy and profilometry. The ATR-FTIR spectra of the plasticized PVC did also change due to the physical interaction between the polyamide fibres and the plasticizer. Furthermore, polyamide fibres were visible on the plasticized PVC surface under optical microscopy and on the 3D profilometric images, which did no occur with cotton nor with polyamide-polyester fibres. Dry cleaners made of mixed polyester-nylon fibers did not show alterations detectable by ATR-FTIR spectroscopy, although visible alteration of the surface was detected by optical microscopy and profilometry at extended cleaning times. Cotton swabs caused physical and chemical alterations due to migration of plasticizer at any cleaning time (Chapters 5 and 7.3), which were detectable by optical microscopy, profilometry and ATR-FTIR spectroscopy. Commercial PVC samples with no plasticizer in their composition showed a different response to the dry cleaning: scratches on the surface were visible with all dry agent cleaners after long cleaning time, being more intense when cotton swabs and polyamide were used (Chapter 7.3).

9.1.2 Surface Topography

As shown in Chapters 5, 7.1 and 7.3, the topography of the PVC surface played an important role in the cleaning. It could be concluded that dry cleaning methods on smooth surfaces produced significant changes in both plasticized and non-plasticized PVC samples when cleaned for long time (see Chapters 5 and 7.3). On the other hand, rough surfaces (such as the doll investigated in Chapters 7.1 and 7.2) were more prone to keep cleanings agents trapped in the heterogeneities of the

surface. The cleaning action, in terms of homogeneity, was also more difficult to control under these circumstances. As explained in the previous section, residues from commercial cleaner Brillianize-Kleenmaster were visible by means of the 3D images obtained by profilometry, when tried on the plasticized PVC doll (Chapter 7.1) due to the irregular and rough surface.

9.1.3 Chemical nature of dirt and degradation products

Dirtiness from natural soiling accumulated on commercial plasticized PVC (Chapters 5) and identified as pollutants, dust, fibers and sand, could be partially removed by dry cleaning agents used in this research. However, differences on the homogeneity were visible by means of the reflection images provided by profilometry. Through these images it could be proven that polyester-polyamide cloths produced the most homogeneous and efficient cleaning compared to polyamide or cotton dry cleaners. In the case of the plasticized PVC doll (Chapters 7.1 and 7.2), dry cleaning methods were completely ineffective, since the dirtiness was not composed of particles deposited on the surface but of organic material such as protein substances, fatty acid or polysaccharides imbued on the plasticized material. In this case, wet cleaning methods were effective, although not to the same extent. Regarding efficiency, noticeable difference where found among them due to the nature of the dirt on the doll. Due to the non-polar nature of proteins and fatty acids, water and alcohol-water mixtures were not very efficient. Organic solvents could have dissolved these compounds but are not to be used due to the risk of extracting plasticizers. However, aqueous solutions formed by Hostapon T and KOH resulted very effective in the cleaning. In the case of the Hostapon T, its anionic nature is able to solvate proteins and lipids, while aqueous KOH solution, due to its strong basic character, produced the hydrolysis of proteins and moderate low acids substances like lipids. In the case of polysaccharides, these can be dissolved easily in aqueous solutions due to their hydrophilic nature.

In terms of homogeneity and strength of the cleaning, KOH solutions produced a large material removal, as evidenced by the high difference between the roughness (measured by the Sq parameter) before and after the cleaning. A significant deep action was also visible in the 3D images and roughness profile provided by profilometry (Chapter 7.1). On the contrary, the cleaning obtained by means of Hostapon T was more homogeneous and more superficial.

The degradation of commercial PVC affected both the bulk polymer and the plasticizers. Polyenes derived from the PVC degradation, while long chain alcohols, benzoates and phthalic anhydride were produced from the photo-ageing of phthalatic acid dialkyl esters used as plasticizer (Chapters 5 and 8). For the removal of these degradation products (Chapter 5), dry cleaning methods resulted insufficient, while wet cleaning methods seemed to be more efficient and provided a more homogeneous cleaning. However, as in the doll's case, different results were achieved among cleaners due to the nature of the compounds produced by the ageing of the plasticized PVC material. This meant, that because of the low polarity of the degradation products, only anionic detergent solution Hostapon T provided an efficient and homogenous cleaning, while polar solutions such as deionized water, ethanol-water 1:2, Multiren or Brillianize-Kleenmaster were ineffective (Chapter 6).

9.2 Degradation investigation

9.2.1 Photo-degradation of the commercial plasticized PVC

From the ATR-FTIR and GC-MS, the following compounds were identified from the photo-ageing process of the commercial plasticized PVC used in the first part of the research:

- alcohols, benzoates and phtalic anhydride resulting from plasticizer degradation,
- alquenes which were produced from the polymer degradation.

In addition, the experimental results showed an increase of C_9 alcohols (almost linear) and phthalic anhydride during the ageing process (not as clear as in the alcohols), while the benzoates' concentration decreased. In order to explain this differences, a Norrish II mechanism has been proposed to explain the formation of alcohols from intermediate benzoates.

ATR-FTIR spectroscopy showed progressive peak formation due to compounds formed at the polymer surface during the artificial photo-ageing process, which was supported by the increase of the absorbance at 400-500 cm^{-1} in the UV-Vis-spectrum. These facts indicated the generation of chromophore groups during the photo-ageing processes, leading to a continued yellowing and loss of gloss of the samples during the ageing process.

Regarding the extent of the degradation process, all the analytical and examination techniques used in this research were in clear agreement: photo-ageing had few effects over the first two weeks, while a significant increment in degradation was noticed after the second week of the photo-ageing process. As this process mimicked outdoor conditions, it can be concluded that the PVC material assessed should not be exposed for more than two weeks to unprotected environments.

9.2.2 Degradation of the plasticized PVC doll

In contrast to the commercial plasticized PVC, the plasticized PVC doll used in the second part of the research showed not only visible dirtiness of the surface, but also evident signs of degradation in form of white particles accumulated on several areas. By means of ATR-FTIR and GC-MS analyses, these particles were identified as a mixture of palmitic ($C_{16:0}$) and stearic acid ($C_{18:0}$), accompanied by 2-ethyl-hexyl esters of fatty acid.

Based on the doll composition and supported by literature, these acids and esters accumulated on the doll surface were identified as internal lubricants migrated from the bulk. Furthermore, the fact that only $C_{16:0}$ and $C_{18:0}$ fatty acids were detected in the surface in comparison to $C_{14:0}$ and $C_{12:0}$ could be due to their higher proportion in the lubricant. In addition, neither migration to the surface nor degradation products from the bis (2-ethyl-hexyl) phthalate were identified.

9.3 General conclusions

As a general conclusion, it can be stated that after a comprehensive investigation and development of the cleaning methodology for artworks made of plastics, several dry and wet cleaning methods specific for plasticized PVC artworks can be proposed as a result of the research. These cleaning methods have been proved not only to be safe for plasticized PVC material, but also efficient at removing dirtiness and degradation products from the material's surface. Furthermore, a new non-destructive method for the quantification of the cleaning efficiency has been presented, as well as a novel approach to the design of tailored cleaning solutions has been successfully accomplished.

9.3.1 Methodology and conservation

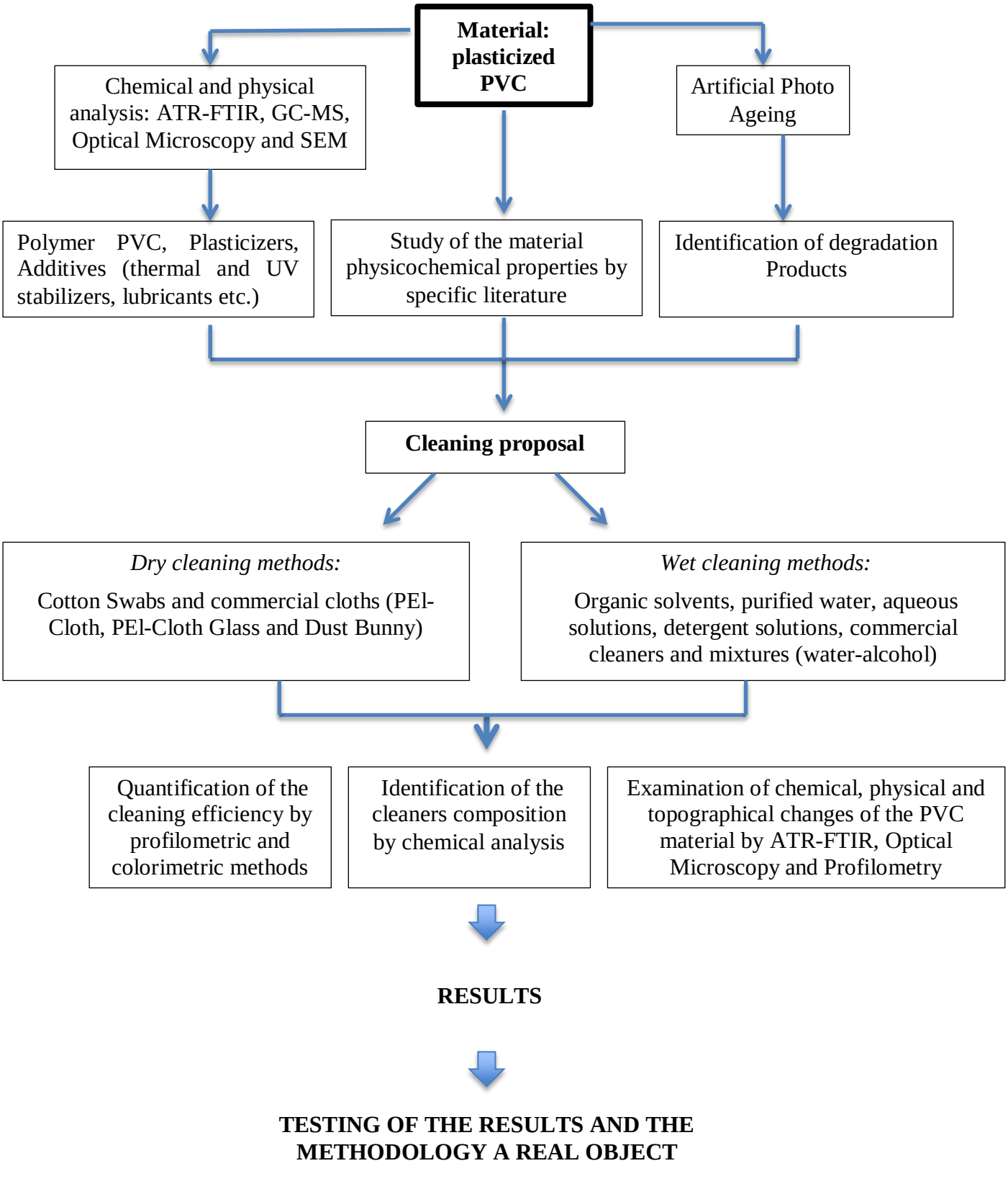
A novel methodology of study proposed for cleaning plastics objects has been successfully applied, demonstrating that specific cleaning agents can be found for a particular plastic material. Subsequently, the steps firstly proposed in the methodology have been followed up for plasticized PVC, achieving suitable and efficient cleaning agents.

In contrast to others researches, no lab-made samples but commercialized plasticized PVC materials have been used for the investigation. This unusual

approach has proven that it is possible for conservators to find cleaning treatments for artworks made of plastics materials, even if the plastic's composition is unknown. Thus, the methodology proposed in this research opens a new way to face the cleaning of plastics objects at museums and conservation centres, since plastics objects at art collections are not always entirely characterized, making it difficult for conservators to find appropriate cleaning methods.

Furthermore, following the methodology of study initially proposed, the cleaning methods discovered by the investigation on commercial plasticized PVC samples were tested on a real plasticized PVC object (doll head) with degradation signs. By means of this "iterative process", safe and efficient cleaning methods were found, what proved the suitability of the methodology on a real case.

Methodology proposed for the investigation of the cleaning of plasticized PVC artworks:



9.3.2. Dry cleaning investigation

- Plasticized PVC was found to be sensitive to both the chemical features of the cleaning agent and the performing time;

- Cloths of the same chemical composition produced similar chemical and physical alterations on both the plasticized and unplasticized PVC;

- At any cleaning time, cleaners composed of polyamide fibres highly interacted with plasticizer in the PVC, as well as cleaning by means of cotton swabs damaged the PVC samples by migrating plasticizer. Therefore dry cleaner agent composed either cotton or polyamide are not recommended for plasticized PVC;

- Dry cleaning by means of polyamide-polyester cloths did not produced any physical and chemical changes at low times on the plasticized PVC tested in this research, although migration of the plasticizer was produced after high cleaning times. Therefore, polyamide-polyester cloths are recommended, under previous controlled testing, for plasticized PVC;

- The FTIR bands ratio 739 cm^{-1} plasticizer / 635 cm^{-1} polymer has been proved to be an useful indicator of the migration of plasticizer PVC when testing dry cleaning agents for plasticized PVC: the higher the ratio, the higher is the migration of plasticizer with the cleaning;

- Change of the FTIR bands ratio PVC crystalline (634 cm^{-1})/PVC amorphous (612 cm^{-1}) has been proved to be a suitable indicator of the modifications in the PVC polymer when using dry cleaning methods;

- From an efficiency point of view, polyester-polyamide cloth cleaners resulted to be the most efficient for the dry cleaning of the plasticized PVC surfaces investigated in this research, compared to cotton swabs and polyamide cloths;

- A direct relation between efficiency and the cloth's texture could not be established by means of the present investigation.

9.3.3 Wet cleaning investigation

- Plasticized PVC morphology was found to be sensitive to both the chemical nature and the concentration of the cleaning agents;

- Organic solvents caused morphological modifications of the plasticized PVC when used pure;

- Both deionized water and basic KOH aqueous solution 1M caused no physical or chemical alterations of the material. However, cleaning with KOH aqueous solutions 1M could cause uncontrolled excessive cleanings, which is not recommended in conservation of artworks. To avoid this, the concentration of the KOH solution must be carefully selected;

- In contrary to the literature, one of the detergents tested in this research seemed to extract plasticizer from the PVC samples when used for long cleaning times, despite the fact that had been recommended for plastics artworks. Therefore, even though detergent solutions may be effectively used for plastics cleaning, these must be tested when applied on plasticized PVC material in order to avoid plasticizer extraction;

- The commercial cleaner specifically formulated for plastics cleaning in conservation did not only show no better response in terms of safety and

efficiency with respect to those of known composition, but seemed to leave residues after its use on rough plasticizes PVC surfaces, which advices to carefully test any commercial cleaner before its use for plasticized PVC cleaning;

- The *"Plasticizer Index"* (PI) (Eq.1) proposed and developed in this research has resulted to be a suitable tool not only for the investigation of the plasticizer migration during wet cleaning treatments, but also for the selection of suitable proportions and performance times when using cleaning solutions composed of several solvents.

(Eq.1) $$\mathbf{PI}\ (\%) = \left(\frac{\left(\frac{A_{1722\ cm^{-1}}}{A_{1426\ cm^{-1}}}\right)_{after\ cleaning} - \left(\frac{A_{1722\ cm^{-1}}}{A_{1426\ cm^{-1}}}\right)_{before\ cleaning}}{\left(\frac{A_{1722\ cm^{-1}}}{A_{1426\ cm^{-1}}}\right)_{before\ cleaning}} \right) \times 100$$

It therefore may be considered as an alternative method to the traditional Hildebrand parameters used to estimate the degree of interaction between materials and solubility. Furthermore, the use of the *"Plasticizer Index"* in the finding of mixtures of organic solvents highly increases the possibilities of the cleaning methods. This is due to the fact that dirt, degradation products or even residues from old restorations are in many cases insoluble in water or detergents and only organic solutions are suitable for their removal;

- Basic KOH aqueous solutions and detergents were the most effective in the removal of incrusted dirtiness in plasticized PVC, while detergent solutions were the most suitable cleaning agents for the degradation products on artificially aged plasticized PVC samples.

As a conclusion from the results obtained in the present research after the testing of dry and wet cleaning methods on new, degraded and soiled plasticized PVC samples, it can be stated that:

1) PVC cleaning has not only to match the chemical composition of the material, but also its topography, its degradation stage and its cleanliness

condition, since these are critical factors affecting the response of the material to the cleaning;

2) It is absolutely necessary to test any cleaning agent before its use on plasticized PVC, since adverse results from the chemical, topographical and physical point of view are likely to occur.

9.3.4. Quantification and evaluation of the cleaning methods

A novel method for the quantification of cleaning efficiency on plastics materials has been found based on proposal of a "Cleaning Efficiency Index", which may be determined by either spectrocolimetric (L* parameter or Lightness in the CIElab space colour) (Eq.2) or profilometric parameters (Sq parameter or standard deviation for the amplitudes of the measured area surface) (Eq.3):

(Eq.2) $$\text{Cleaning Efficiency } (\%) = \left(\frac{L^*_{cleaned} - L^*_{soiled}}{L^*_{unsoiled} - L^*_{soiled}}\right) \times 100$$

(Eq.3) $$\text{Cleaning Efficiency } (\%) = \left(\frac{Sq_{cleaned} - Sq_{soiled}}{Sq_{unsoiled} - Sq_{soiled}}\right) \times 100$$

The higher the value of the Cleaning Efficiency Index, the more efficient is the cleaning. Therefore, by the application of these equations it is possible to compare several cleaning methods and determine their efficiency, which can help conservators decide for the most efficient cleaning methods. Comparing both indexes, it can be stated that cleaning efficiency calculated by profilometric methods shows a few advantages over calculations based on spectrocolorimetry. These advantages refer to the versatility of the profilometric technique, which can be used on any type of surface, regardless the object size, volume or topography, as well as being a non-contact technique, contrary to Colorimetry, where the measurement device needs to be in contact with the object. Furthermore, colorimetric quantification depends on the contrast between dirtiness and substrate, which is a disadvantage with respect to profilometric techniques. On the contrary, colorimetry is more economic and user

friendly compared to profilometry, which makes it affordable for any conservation and research center.

Regarding the microscopic techniques used in this research for the examination of the cleaning methods, optical microscopy has resulted to provide complementary information to quantification techniques such as colorimetry or profilometry. Thus, by means of optical microscopy, a first identification of the cleaning efficiency could be obtained for either degraded or soiled material, providing valuable information for the assessment of the cleaning in the museum environment. In contrast to microscopic techniques such as optical microscopy or scanning electron microscopy, profilometry yields not only 2D and in focus 3D images, but also surface roughness profiles. The 3D images provided by profilometry are at the millimeter scale, while sub-micrometer scale can be achieved by SEM microspopy. The fact that that profilometry does not need any sampling from the object (contrary to SEM) and can be used in non contact mode makes this technique perfectly suitable for the examination of the cleaning effects in a museum environment. Furthermore, 3D images and roughness parameters provided by profilometry have been revealed to be a significant tool to assess topographical changes on plastic surfaces during the cleaning and an alternative way to chemical analyses (ATR-FTIR spectroscopy) to detect residues left by cleaning agents. At last, profilometry has also been proven to be an additional technique to assess the intensity and homogeneity of the cleaning process by means of the analysis of the roughness profiles and 3D images before and after the cleaning treatments, what can definitively be of a valuable help for conservators.

Furthermore, ATR-FTIR technique has been used in this research to gather both qualitative and quantitative information from the dry and wet cleaning methods tested on both commercial and non-commercial PVC. Comprehensive qualitative information has been provided by the ATR-FTIR analyses along the wet and dry cleaning experiments, which can be summarized as:

- identification of PVC polymer and plasticizers,

- identification of dirtiness compounds,
- identification of dry cleaner compositions,
- identification of residues left by the cleaners agents on the samples,
- identification of the IR bands corresponding to the functional groups of the dirt before and after the cleaning, which could be used as a qualitative assessment of the cleaning efficiency,
- identification of chemical and physical modifications of the PVC as a consequence of the cleaning,
- investigation of the alterations of the crystallinity in the PVC material due to the cleaning, by means of the A634/A612 ratio between the C–Cl intensities of the PVC crystalline and amorphous bands,
- investigation of the plasticizer migration from the PVC polymer as a consequence of the cleaning, by means of the A739/A635 ratio between the C–H plasticizer and the C–Cl PVC resin bands.

Furthermore, quantitative information regarding the cleaning effects on plasticized PVC was also gathered by means of the "Plasticizer Index" (Ed.1), already mentioned in section 5.3. This equation is based on the ratio of the peak intensities of the plasticizer carbonyl band and the PVC C–H band before and after the cleaning treatments $\left(\frac{A_{1722\ cm^{-1}}}{A_{1426\ cm^{-1}}}\right)$.. The decrease of the Plasticizer Index (expressed as %) represents the loss of plasticizer in the PVC polymer due to the cleaning action.

On the other hand, since ATR-FTIR technique is a surface analysis technique, the effects of the cleaning inside the bulk polymer, such as the plasticizer leaching or the penetration of the cleaning agents into the polymer, could not be assessed. However, when samples were weighed after cleaning, weight variation could not be appreciated since the cleaning was only superficial and for short times. Weight variations were only detectable after immersion in the cleaning solvents, due to the extraction of a measurable amounts of plasticizer.

9.3.5. Degradation products and cleaning

Chromatographic (GC-MS and LC-MS) and spectroscopic techniques (ATR-FTIR) have been proven to be efficient for the investigation and identification of products produced on plasticized PVC objects as a consequence of degradation or ageing processes. The information gathered by these techniques provide a better understanding of the chemical degradation of the material, helping the conservator to find suitable and specific cleaning methods according to the degradation status of PVC. However, there are significant differences between both techniques that may be taken into account when working in the museum environment. In the case of ATR-FTIR spectroscopy, the penetration on the sample is only of a few microns and samples do not need any preparation. These characteristics made ATR-FTIR technique suitable for the investigation of the cleaning process occurred on the surface of any PVC materials in museums collections. However, when a deeper identification of the cleaning effects in the bulk material or the detailed composition of the degradation products is needed, ATR-FTIR spectroscopy becomes insufficient. In these cases, chromatographic techniques should be used, which has to be carefully assessed, due to the need for sampling. On the other hand, XPS as analytical technique used in the current investigation has proven to provide valuable information regarding elementary composition, which has helped to the initial identification of additives in the plastics. However, this technique is not recommendable for the study of plasticized PVC, due to the damage that evaporated plasticizer (relatively high vapor pressure) can produce within the XPS equipment. Furthermore, the investigation of the physical changes on the PVC material due to the photo-ageing has been successfully investigated by means of colorimetry, gloss measurement and UV-Vis Spectroscopy. These techniques have provided information complementary to the chemical analysis, helping to understand the rate of the degradation process over time by means of the monitoring of: colour, gloss and "chromophore group" formation in the plasticized PVC material.

Regarding degradation, double carbon bonds were formed in the polymer of the commercial plasticized PVC by a typical dehydrochlorination process, which produced the yellowing of the material. Furthermore, the main plasticizer (DINP) was identified to degrade into C9 alcohols and Phthalic Anhydride through a Norrish II reaction. However, the degradation ratio of the material was proven to be not linear over time by means of the qualitative and quantitative experiments. The ageing process was particularly slow during the first and second week, then a high increase of the photo-degradation was noticeable. This change of the degradation kinetics was due to the progressive decrease of the efficiency of the photo-ageing stabilizers identified in the polymer, producing chemical and physical alterations, such as colour change and gloss loss. Eventually, the photo ageing process led to the formation of a superficial layer of degradation produces on the polymer surface that was visible to the naked eye.

On the contrary, the degradation in the plasticized PVC doll was not the result of a homogeneous ageing of the total surface, but the migration of internal lubricants from the bulk to specific areas. Additionally, no degradation products from bis (2-ethyl-hexyl) phthalate could be identified, confirming that the phthalate plasticizer in the doll did not undergo degradation as the one in the commercial plasticized PVC. Therefore, the degradation pathways were proven to obey to different causes in both plasticized PVC materials.

From a conservation point of view, the necessity of the correct identification of the degradation products in order to select appropriated cleaning methods for the removal of the diverse products obtained by the ageing and degradation of PVC materials has been proven. On the other hand, the degradation stage of the plasticized PVC has to be considered, since the rate in which the degradation products are formed will be different in each phase of the degradation process, which in turn will condition the appropriate cleaning method. As a result of the present research, dry cleaning methods resulted ineffective in the removal of degradation products and migrated additive, while wet cleaning methods produced a

better and more homogeneous removal of the severe degradation products formation.

9.4 Future investigations

It must be taken into account that, further investigations with regards to the behavior of the material after the cleaning would be advisable. In this way, the monitoring of the cleaning with time could provide conservators with valuable information such as:

a) time passed until a new cleaning is needed,

b) information about adverse consequences due to the cleaning treatments,

c) information about the consequences due to the removal of degradation products from the plastic surface.

Even though the contribution of the present study is limited to PVC, the mid-term objective for future studies aims at the establishment of well understood, commonly applied and effective methods to face cleaning and conservation of plastic objects forming part of our cultural heritage. For this, the application of the methodology developed in this research to other plastics of interest in the museum environment, such as polyesters, polyurethane or poly (methyl methacrylate) (PMMA), should be the next step in the investigation of plastics cleaning.

10. LITERATURE

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11. INTRODUCCIÓN

11.1. Polímeros.

Desde un punto de vista general, "los materiales plásticos, antes de añadir aditivos, son moléculas muy grandes compuestas de repeticiones de pequeñas partes. En el caso de algunos materiales de origen natural, tales como el betún, la goma laca y el ámbar, la composición es heterogénea y compleja pero en todos los otros casos, los materiales plásticos pertenecen a una familia química conocida como *grandes polímeros*" (Brydson, 1999). Así, los plásticos están relacionados con polímeros, pero ¿qué es un polímero? Etimológicamente hablando, la palabra polímero viene del griego antiguo y significa "muchos-partes". Bajo ciertas condiciones, la combinación de partes más pequeñas, monómeros, forma la molécula de polímero en sí, que puede tener diferentes tamaños, dependiendo del número de monómeros o el grado de polimerización (Chanda y Roy, 1998). Mientras que todos los plásticos son polímeros, no todos los polímeros son plásticos. Polímeros incluyen plásticos y cauchos, así como muchos compuestos poliméricos naturales.

Normalmente hay tres estados físicos o estados de agregación: sólido, líquido y gaseoso. Moléculas simples pueden cambiar de un estado físico a otro a una temperatura fija, que varía de acuerdo a la sustancia. Dentro de los polímeros sin embargo, los cambios de estado están menos definidos y pueden ocurrir en un rango de temperatura (Brydson, 1999). De acuerdo con su estructura macromolecular y sus propiedades físicas dependientes de la temperatura, los polímeros se dividen en tres categorías principales: termoplásticos, elastómeros y termoestables. A diferencia de los primeros, termoplásticos, polímeros que pueden ser calentados y remodeladas, los elastómeros y los termoestables no cambian con la temperatura una vez que se han formado o fabricados. Sin embargo, los elastómeros y los termoestables difieren en la elasticidad, ya que los elastómeros son suaves y los termoestables no lo son.

Por otro lado, si se analiza la estructura química y el grado de entrecruzamiento dentro de las moléculas, los polímeros termoplásticos, elastómeros y termoestables tienen características muy diferentes. Como se muestra en la Figura 1 (Menges, 1996), las estructuras termoplásticas pueden ser lineales o ramificadas, sin entrecruzamiento en las cadenas macromoleculares, mientras las macromoléculas elastómeras y termoestables tienen cadenas laterales con estructuras complejas: de bajo entrecruzamiento en el caso de elastómeros y de alto grado de entrecruzamiento en termoestables.

En los termoplásticos, la estructura macromolecular viene dada por la estructura química de las unidades de monómero, el orden de las unidades de monómero en la cadena molecular y las cadenas laterales existentes (Klein, 2011). Dependiendo del orden de las moléculas en el polímero, los termoplásticos se dividen en dos grupos: amorfos (donde las cadenas poliméricas están distribuidas al azar) y cristalinos (donde existe un cierto grado de orden en medio de las cadenas poliméricas).

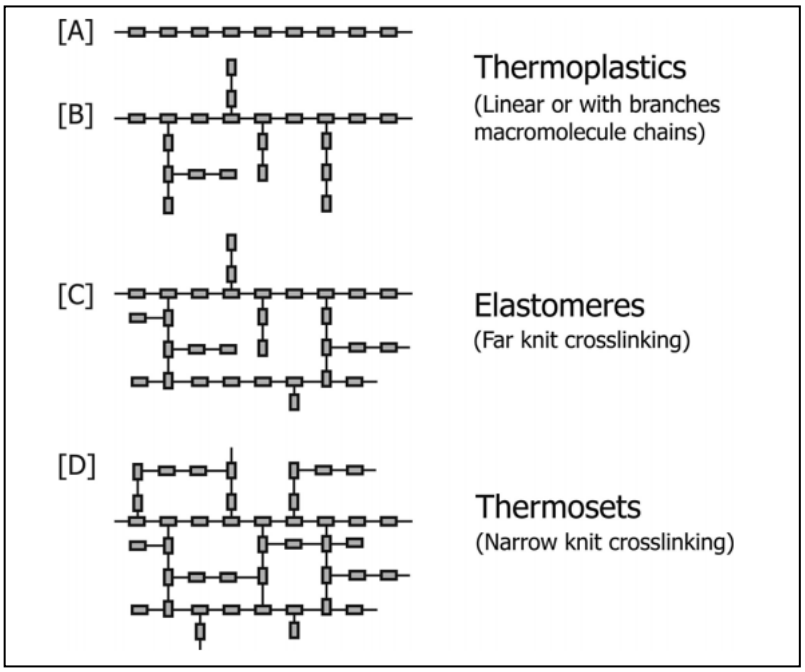


Figura 1: Tipos de polímeros y estructura.

Los polímeros utilizados en plásticos modernos son principalmente sintéticos. Sin embargo, los polímeros naturales, sintetizados por organismos también existen y se han utilizado desde la antigüedad, como por ejemplo, el betún, el cuerno, el marfil, la concha de tortuga, la celulosa o la caseína (García Fernández-Villa, 2010).

Desde un punto de vista conceptual, "los plásticos" son materiales versátiles que pueden ser modelados en una gran variedad de formas y texturas, siendo utilizados como sustitutos de otros materiales (marfil, madera etc.) o en combinación con otros materiales, como por ejemplo en los conglomerados de madera y resina, polyester reforzado de fibra de vidrio etc. Una amplia variedad de objetos plásticos ampliamente presente en nuestra vida diaria (por ejemplo muebles, juguetes, cubiertos, etc.) ahora se encuentran en museos y colecciones de arte como recuerdos de nuestro pasado reciente (Figura 2) (Mills, 2005). En otros casos, los artistas hacen uso de materiales plásticos nuevos o reciclados para la creación de obras de arte dado que a través del material pueden expresar sus sentimientos y emociones.

Figura 2. "Boca abierta, enseñando los dientes", 2000. Reproducida con permiso de *William and Ruth True collection*.

Mirando hacia atrás en la historia, no fue sino hasta el siglo XX que los compuestos fenólicos se convirtieron en la primera resina totalmente sintética con éxito comercial y el celuloide se convirtió en el primer material plástico obtenido

mediante la modificación química de un polímero (Brydson, 1999). Los polímeros semi-sintéticos y sintéticos fueron creados y utilizados para imitar materiales naturales caros y escasos, como el marfil o la concha de tortuga, que no estaban al alcance de la mayoría de la población. De esta manera, "materiales de lujo" podrían ser sintetizados y hacerse más ampliamente disponibles para el consumo.

Uno de estos materiales es el acetato de celulosa, un plástico sintético a base de algodón que se comercializa como *Secoidin* a principios del siglo XX. Otro plástico sólido importante fue la baquelita (una resina de fenol-formaldehído), descubierta por el químico belga Leo Baekeland (Quye y Williamson, 1999) y cuyo uso se hace popular en la década de 1920. Durante las décadas de 1930 y 1940 comenzó el amplio uso industrial de los plásticos y así se sintetizaron cuatro de los principales termoplásticos de hoy en día: poliestireno (PS), cloruro de polivinilo (PVC), las poliolefinas (por ejemplo el prolipropileno PP o el polietileno PE) y el polimetilmetacrilato (PMMA) (Brydson, 1999).En la década de 1950, los plásticos fueron fabricados como fibras, contribuyendo a un enorme desarrollo de nuevos textiles. También los juguetes y los objetos domésticos fueron fabricados con material plástico, siendo introducidos como objetos de la vida cotidiana. En los años 1960 y 1970, los plásticos comenzaron a ser usados como parte de muebles, barnices y pinturas, como las pinturas de acrílico al agua. Desde la década de 1980 hasta ahora, la diversidad de plásticos ha crecido continuamente, formando parte de materiales de alto rendimiento utilizados en dispositivos médicos, la industria aeroespacial, la nano y biotecnología, etc.

En ambos casos, conceptualmente e históricamente, debido a su relativamente reciente descubrimiento y desarrollo, solamente constituyen la materia prima para objetos relativamente modernos, un menor de edad. Aunque una parte cada vez más importante de las colecciones de los museos (Mills y White, 1994).

11.2. Cloruro de polivinilo (PVC).

El cloruro de polivinilo (IUPAC Polychloroethene) comúnmente abreviado como PVC, es un polímero termoplástico utilizado muy ampliamente que fue descubierto accidentalmente en el siglo nonagésimo por dos investigadores: el físico y químico francés Henri Victor Regnault en 1838 y el alemán Eugen Baumann en 1872. Sin embargo, no fue hasta 1913 cuando el químico alemán que trabaja en IG Farben AG, Friedrich Heinrich August Klatte, patentó un proceso para la polimerización de PVC para la producción de fibra.

Se basa en la adición de peróxido directamente al monómero y completando el endurecimiento del polímero usando la luz del sol. No obstante, el material se mantuvo como una curiosidad científica durante más de una década, ya que las fibras eran de muy mala calidad y el PVC puro es inmanejable y térmicamente inestable.

11.2.1. El desarrollo industrial y presencia en las colecciones de arte.

El interés comercial del cloruro de polivinilo se reveló por las diferentes patentes presentadas de forma independiente en 1928 por el Carbide y Carbon Chemical Corporation, Du Pont e IG Farben (Brydson, 1999), pero el avance más importante se produjo en los Estados Unidos, cuando la empresa BF Goodrich contrató al científico industrial Waldo Semon para desarrollar un sustituto sintético para el caucho natural, cada vez más costoso. Semon descubrió que las propiedades de PVC pueden ser modificadas cuando se polimeriza con diferentes disolventes tales como cloronaftaleno, éter o-nitrodifenil, fosfato de tricresilo, el benzoato de bencilo o ftalato de dibutilo (Semon, 1932, 1937), produciendo un material rígido parecido al caucho después del enfriamiento. La adición de estos "plastificantes" produce un material que a temperaturas de fusión aceptables puede ser procesado a productos que eran de forma permanente suaves y flexibles. Al mismo tiempo los primeros

estabilizadores térmicos comenzaron a ser utilizados en composiciones de PVC (Leadbitter *et al.*, 1994). Durante la década de 1950 muchas empresas más comenzaron a fabricar PVC y los volúmenes de producción de este polímero se incrementaron extraordinariamente en todo el mundo durante el siglo 20, hasta convertirse en el segundo polímero más importante a nivel mundial (Menges, 1996) (Figura 3).

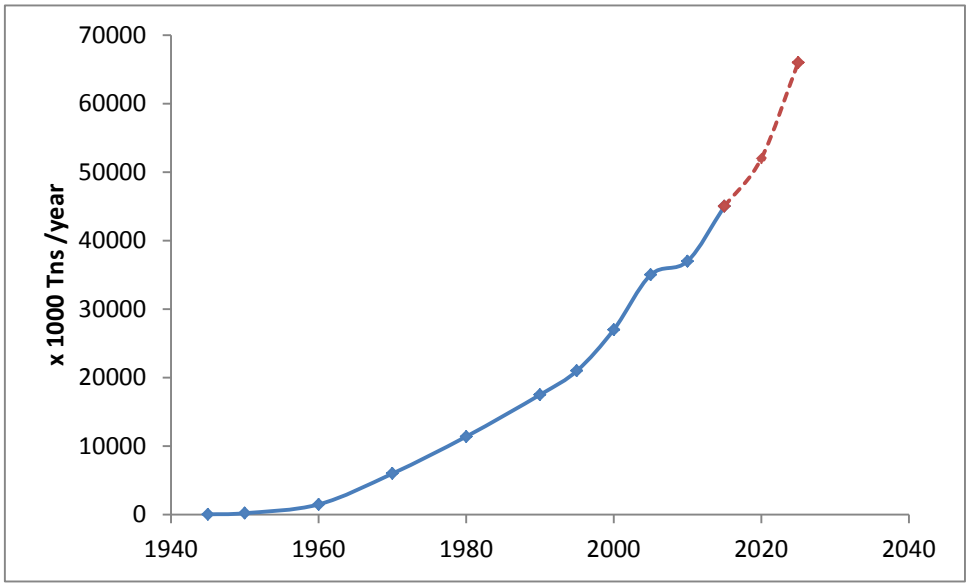


Figura 3. Consumo de PVC anual en Europa del oeste desde 1970.

Como característica particular, el PVC es uno de los pocos polímeros que son insolubles en su monómero, lo que da la posibilidad de controlar la morfología durante polimerización mediante el uso de tensioactivos en la interfase polímero/monómero. En cuanto a la polimerización en cadena de PVC, hay tres tipos principales diseñados para producir resina de vinilo de diferente tamaño de partícula y morfología: *suspensión*, *emulsión* y *en masa* (Kutz, 2011). Actualmente, el proceso de *suspensión* está dominando la producción de PVC industrial, representando alrededor del 75% de la capacidad de fabricación de PVC en el mundo (Mishra and Yagci 1998).

Durante el proceso de polimerización en *suspensión*, se emplean una agitación muy exhaustiva junto con altos cantidades de productos químicos y dispersantes

para suspender gotas de monómero de cloruro de vinilo (VCM) en agua durante la polimerización. Esto produce una suspensión de granos de PVC en agua que tiene un tamaño medio de grano generalmente entre 120 y 150 micras. El proceso consiste en cuatro etapas básicas: polimerización, decapado para eliminar el VCM residual, centrifugación para eliminar el agua y secado (Wilkes *et al.*, 2005). Alternativamente, la polimerización en emulsión y en masa son las tecnologías menos empleadas para la fabricación de PVC. La polimerización en emulsión se utiliza para producir resinas especiales para aplicaciones de pasta (Mishra y Yagci, 1998), produciendo un polvo de tamaño de partícula pequeño con muy pocos monómeros libres. La polimerización en masa produce un PVC muy similar a la obtenida por el proceso de suspensión, pero con más la porosidad de las partículas. Ambas técnicas comprenden sólo una pequeña fracción de la producción global de PVC (Kutz, 2011). El polímero de cloruro de vinilo se puede combinar con otras materias primas para formar una "composición" o "compuesto", siendo los aditivos plastificantes más importantes en PVC. En la industria, el PVC ha sido ampliamente utilizado para diferentes tipos de aplicaciones, como la construcción, los cables, la industria del automóvil, electrodomésticos, dispositivos médicos, envases, etc. Desde un punto de vista cuantitativo, los principales usos de PVC son en tuberías y accesorios (35%), películas y hojas (15%), los materiales del suelo (10%), alambres y cables aislantes (5%), piezas de automóviles (5%) y los adhesivos y recubrimientos (5%) (Chanda y Roy, 1988).

A pesar de la importancia del PVC en la industria, su papel como material utilizado en el arte y el diseño se debe también tenerse en cuenta. Como muchos otros plásticos, el PVC ofrece el proceso de creación con una libertad que no ofrecen materiales tradicionales como piedras o cerámica, y que ha permitido a los diseñadores a cambiar el curso de diseño de moda (Quye y Williamson, 1999).

Como resultado, se pueden encontrar "objetos icónicos de PVC" en museos y colecciones de arte como ejemplos de piezas que se han creado como objetos ordinarios, pero cuyo éxito les hizo único y atemporal. Por ejemplo, el mundialmente

conocido "Silla Hinchable" de los diseñadores De Pas, D'Urbino, Lomazzi y Scolari (figura 4) es hoy en día parte de las colecciones de arte contemporáneo como el MOMA (Nueva York) y el Museo Victoria and Albert (Londres). A partir de mediados de siglo XX, los artistas han utilizado material de PVC para la creación de objetos de arte, como la obra "Bandera", realizado por el artista danés Peter Louis-Jensen en 1969 (Lundbye y Cone, 2013) o la recientemente restaurada "aeromodeller 00- PL "(1969-1971), realizada por el artista belga Paramarenko, que se ha convertido en un paradigma de PVC en el arte (Huys y van Oosten, 2005).

Figure 4: Silla hinchable, 1967. Diseñadores: De Pas, D'Urbino, Lomazzi y Scolari.
Fotografía cortesía de Zanotta spa (Italy).

Además, el material PVC se ha utilizado no sólo para la creación de objetos imaginativos, sino también para el rendimiento de las instalaciones complejas donde los visitantes están destinados a interactuar directamente con la obra (Figura 5). Por lo tanto, se puede afirmar que el PVC forma parte de nuestro patrimonio cultural, ya

sea como objetos procedentes de nuestro pasado reciente o como las creaciones artísticas más actuales.

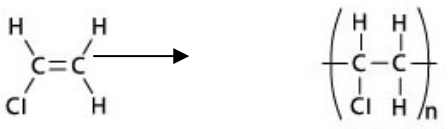
Figure 5: Victorine Müller: "Ballon Stratosphérique". Foto cortesía de la artista.

11.2.2. Propiedades químicas, físicas y mecánicas.

El PVC es un polímero termoplástico compuesto por 58% en peso de cloro, más 42% en peso de hidrocarburos (Wilkes *et al.*, 2005). El PVC, que a menudo se suministra en forma de polvo, se mezcla con una gran diversidad de compuestos tales como aditivos, pigmentos, plastificantes, etc. Para su producción industrial moderna, el primer cloro educto se produce por electrólisis de salmuera, mientras que la segunda, etileno, rendimientos del craqueo a vapor en procesos petroquímicos (Leadbitter *et al.*, 1994).

El etileno es entonces tratado con cloro, ya sea directa o a través de una oxi-cloración, y el dicloruro de etileno resultante se térmicamente agrietado de VCM gaseoso (monómero de cloruro de vinilo): CH_2=CHCl. El cloruro de polivinilo se

obtiene de la polimerización del cloruro de vinilo monómero por mecanismos de radicales libres a temperaturas generalmente entre 40 y 70ºC (Kutz, 2011, Leadbitter *et al.,* 1994):



Monomero Polímero

Como el PVC es insoluble en monómero de cloruro de vinilo, la polimerización es un proceso heterogéneo. La fase de polímero se separa de la fase de monómero cuando la conversión alcanza el 0,1% y la polimerización se produce tanto en la fase de monómero como en la fase de polímero. El volumen de la fase de monómero disminuye a medida que la fase de polímero crece y absorbe el monómero. A una mayor conversión del monómero, continúa polimerizando en la fase rica en polímero (Mishra y Yagci, 1998).

De acuerdo con la facilidad de la escisión homolítica del enlace π en el monómero, la polimerización radical se lleva a cabo en presencia de sistemas de iniciación adecuados. Para la producción de radicales libres disponibles para la polimerización de VCM, se utilizan normalmente tres métodos: a) disociación térmica de azo o compuestos peroxo (por ejemplo peróxido de dioctanoilo y peroxidicarbonato de diacetilo), b) los procesos de oxidación-reducción y c) metal alquilos en conexión con el oxígeno (Kricheldorf *et al.*, 2004).

La polimerización por radicales libres de monómeros de vinilo incluye la iniciación de la cadena, propagación, transferencia de cadena a monómero y reacciones de terminación bimolecular. Sin embargo, hay fuertes indicios de que, en la polimerización por radicales libres de VCM algunas reacciones implican mecanismos cinéticos complejos (Asua, 2007), como se muestra en la siguiente secuencia (Mishra y Yagci, 1998):

Iniciación	—> 2R•
Propagación	
Propagación de cabeza a cola	₁ + M —> P•$_{n+1}$
Propagación de cabeza a cabeza	₁ + M —> P*$_{n+1}$
Reacción de desplazamiento del cloro	$_n$ —> (P*$_n$)´
Propagación de cola a cola	$_n$ + M —> P•$_{n+1}$
Formación de ramificaciones de clorometilo	*$_n$)´+ M —> P•$_{n+1}$
División del radical de cloro	*$_n$)´ —> M_n + Cl•
Iniciación de los radicales poliméricos por los radicales clorados	' + M —> P•$_1$
Transferencia de los radicales de cloruro al polímero	₁ + Cl• —> P´$_n$ + HCl
Propagación hacia la formación de una cadena de ramificación	₁ + M —> P•$_{n+1}$
Formación de un doble enlace interno	₁ + M —> Cl•
Tranferencia de la cadena al polimero	₁ + M_m —> M•$_n$ + P•$_m$
Formación de ramificaciones de cadena larga	₁ + M —> P_{n+1}
Final	
Combinación	₁ + P•$_m$ —> M_{n+m}
Desproporcionación	₁ + P•$_m$ —> M_n + M_m
Final del radical primario	₁ + R• —> M_n
Final con radical de cloruro	₁ + Cl• —> M_n

En general, una cadena PVC consta de alrededor de 1.000 unidades de monómero, que normalmente se sintetiza mediante la adición de cabeza a cola. El crecimiento de la cadena se realiza rápidamente y el último paso es la finalización del crecimiento de la cadena, en su mayoría por reacción de transferencia radical de monómero. El radical del monómero es capaz de iniciar una nueva cadena (Kricheldorf *et al.*, 2004). Sin embargo, cuando se produce además de cabeza a cabeza, el extremo inestable de la cadena en crecimiento se reorganiza para producir un doble enlace terminal y un átomo de cloro (Figura 6). Y puesto que el átomo de cloro es un radical libre, se inicia la polimerización de otra cadena (Kutz, 2011).

La transferencia de cadena y el peso molecular están controladas por la energía de activación de la adición de cabeza a cabeza, y por lo tanto se polimeriza por sí solo, lo que hace del PVC el único polímero comercial importante donde la

temperatura de polimerización controla el peso molecular y la distribución del peso molecular (Kutz, 2011).

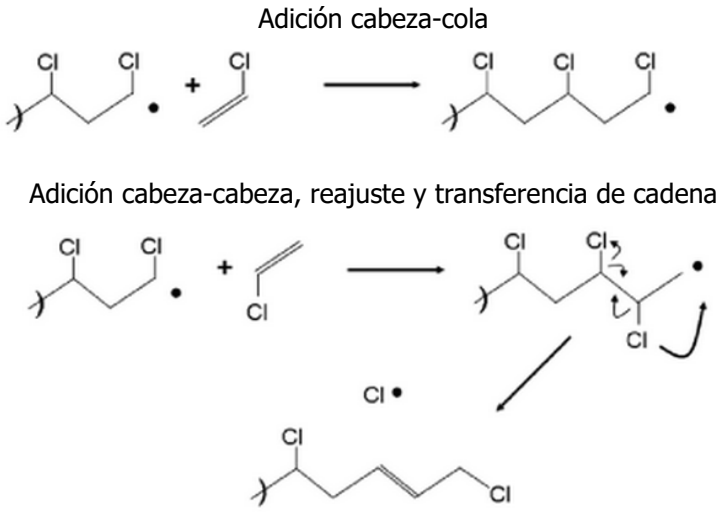


Figura 6: Adición de VCM para el crecimiento de la cadena de PVC.

En cuanto a su estructura química interna, el cloruro de polivinilo contiene tres tipos básicos de enlaces: C--C, CH y C-Cl, cuyas propiedades promedio se muestran en la Tabla 1 (Wypych, 2008).

Tabla 1: Propiedades de los enlaces del PVC.

Enlace	Longitud, pm	Radio, pm	Momento dipolar, Debye
C-C	154	77	0
C-H	109	3	0.40
C-Cl	177	99	1.46

Las resinas de PVC muestran una distribución al azar de pesos moleculares y, por tanto, los valores numéricos están expresados en términos de media. Dependiendo de la aplicación, el peso molecular del PVC (Mw) oscila entre 39.000, utilizado para el moldeo por inyección de piezas de paredes delgadas, a 168.000, que se utiliza para el PVC plastificado (Wilkes et al., 2005). Además, las partículas de

polímeros de PVC cubren una amplia gama de tamaños, como se muestra en la Tabla 2 (Leadbitter, 1994).

Tabla 2: Tamaños de partícula del PVC.

Polímero	Tamaño de partícula (microns)	Rango (microns)
Unseeded emulsion latex	0.1	0.01-0.2
Seeded emulsion latex	1.0	0.1-3.0
Microsuspension latex	1.0	0.2-2.0
Emulsion polymer	40-50	0.1-100
Mass polymer	100-150	80-200
Suspension polymer	100-150	50-250

Como polímero, el cloruro de polivinilo es lineal y sustancialmente termoplástico, donde la presencia del átomo de cloro provoca un aumento en la atracción interna en la cadena y por lo tanto un aumento de la dureza y la rigidez del polímero. Además, los átomos de cloro en la cadena de hidrocarburo conduce a altas fuerzas de valencia secundaria polares, que son responsables de la relativamente alta temperatura de congelación, en el rango de 80 a 90ºC (Menges, 1996).

La cristalinidad de los polímeros depende de la estructura y los enlaces secundarios dentro de la molécula: a mayor regularidad estructural y simetría de las moléculas de polímero y cuanto más fuerte sean las fuerzas secundarias, mayor será la tendencia a la cristalización (Chanda y Roy, 2006). Por medio de estudios de rayos X se ha comprobado que el polímero de cloruro de vinilo, de la manera que se prepara normalmente en los procesos comerciales, es sustancialmente amorfo, aunque presenta una pequeña cantidad de cristalinidad (alrededor de 5%) (Brydson, 1999). El grado de cristalinidad afecta a muchas propiedades, tales como la densidad, fusión, resistencia a la tracción y alargamiento. Además, la cristalinidad está relacionada con el envejecimiento físico, ya que la calidad de los cristales influye en la estructura de la fase amorfa, que es responsable de los fenómenos de

envejecimiento (Wypych, 2008). La cristalinidad en los polímeros a granel puede ser clasificada como "de cadena extendida y la cadena plegada". En polímeros con plegamiento de la cadena, las cadenas poliméricas se pueden plegar de manera regular para formar cristales en forma de placas llamadas laminillas, mientras la cristalinidad de cadena extendida surge en muchos polímeros con estructuras muy regulares (Mitchell, 2004). Polímeros tales como polivinilos, poliamidas y poliésteres son mucho más fáciles de cristalizar que los polímeros reticulados o ramificados, aunque no se suelen cristalizar al 100% y se convierten en polímeros semicristalinos. Se cree que la disposición de cadenas en regiones cristalinas se debe a una combinación de cadenas plegadas y extendidas (Bronzino, 2006).

El orden estereoquímico de los grupos sustituyentes en una cadena de polímero (tacticidad) puede dar tres estructuras distintas: *isotáctico*, cuando todos los grupos están en el mismo lado de la cadena del polímero; *sindiotáctico*, cuando los grupos se distribuyen alternativamente en la cadena y *atáctico*, en donde los grupos están distribuidos al azar en la cadena polimérica. Los polímeros de vinilo (-CH_2-CHX-) puede tener los tres posibles arreglos de grupos laterales (X): atáctico, isotáctico y sindiotáctico. Si los grupos secundarios son pequeños y las cadenas son lineales, el polímero cristaliza fácilmente. Los polímeros isotácticos y sindiotácticos generalmente cristalizan incluso cuando los grupos laterales son grandes (Bronzino, 2006).

Debido a que el cloruro de vinilo no es una molécula simétrica podría tener tacticidad explícita. Sin embargo, en la práctica, el PVC no tiene tacticidad regular, debido a que el extremo en crecimiento de la cadena es un radical libre en un centro de carbono hibridado sp^2, que puede girar libremente. Esto aumenta las tasas de rotación con la temperatura. Por lo tanto, puede obtenerse un polímero más sindiotáctico mediante la polimerización de cloruro de vinilo a muy bajas temperaturas (Kutz, 2011). Los estudios que utilizan técnicas de NRM indican que el PVC convencional es aproximadamente 55% sindiotáctico y el resto en gran medida atáctico (Brydson, 1999). En el PVC, los grupos laterales son grandes (Cl) y

distribuidos al azar a lo largo de la cadena (atáctico), por lo que se forma una estructura no cristalina. Debido a la polaridad relativa del PVC, sólo los líquidos polares pueden penetrar y disolverlo (Menges, 1996). Además, se ha sugerido que el PVC es capaz de actuar como un donante de protones débil y por lo tanto son eficaces los disolventes aceptores de protones débiles (Brydson, 1999). Además, por medio de espectroscopia IR se pueden detectar regiones cristalinas y amorfas, así como el cambio en la cristalinidad puede ser cuantificado mediante la medición de la relación de picos específicos. Es decir, las bandas CH_2 en 1426 cm^{-1} y 1435 cm^{-1} representan regiones amorfas y cristalinas respectivamente (Denizligil y Schnabel, 1994).

Tabla 3: Propiedades físicas y mecánicas del PVC

Property	**Value**	**Unit**
Density	1.35-1.45	g/cm^3
Thermal Coefficient of Expansion	80	$K^{-1} \times 10^{-6}$
Young's Modulus (Stiffness)	2.5-4.1	10^3 MPa
Temperature of use	-15-60	^oC
Specific weight	1.38 – 1.24	g/cm^3
Tensile Strength	40-60	N/mm^2
Glass Transition Temperature (T_g)	81	^oC
Crystalline Melting Temperature (T_m)	212	^oC
Brittleness Temperature	> 23	^oC

Otras propiedades físicas del PVC por ejemplo, son su baja combustibilidad, debido a su alto contenido de halógeno (57%), y su ductilidad y dureza (Lampman, 2003). Como resumen en la Tabla 3 se recogen algunas de las principales propiedades físicas y mecánicas del polímero de PVC. (Brydson, 1999; Wilkes, 2005; Chanda and Roy, 2006; Klein, 2011).

11.2.3. Plastificantes y aditivos

El polímero de PVC es un material incoloro rígido con estabilidad térmica limitada (Brydson, 1999) que se degrada rápidamente a las temperaturas requeridas para el procesamiento (Leadbitter *et al.*, 1994). Con el fin de hacer que sea adecuado para su uso, se deben añadir compuestos que cambian sus propiedades. Al añadir diferentes compuestos tales como plastificantes, estabilizadores térmicos y de UV, lubricantes, y cargas se obtiene una amplia gama de productos de PVC de diferentes características. Otros productos ocasionalmente utilizados son retardantes del fuego, modificadores de impacto o absorbentes de UV y antioxidantes (Tabla 4) (Leadbitter, 1994; Chanda and Roy, 1998; Brydson, 1999; Titow, 1984).

Tabla 4: Aditivos del PVC.

PVC Additives
Stabilisers: Lead compounds, organotin compounds, CaZn stabilisers etc.
Plasticizers: Phthalic acid esters, phosphoric acid esters etc.
Lubricants: Stearic acid, paraffin wax etc.
Impact Modifiers: Toughening agents, e.g. ABS (acetonitrile butadiene styrene), MBS (methacrylate butadiene styrene), EVA (ethylene-vinyl acetate copolymer), ACE (acrylate polymethacrylate copolymer) etc.
Fillers: Calcium carbonate, china clay, talc etc.
Fire retardants/smoke suppressants: Aluminium trihydrate, zinc borate etc.
Colorants: Pigments and dyestuffs.
Antistatic Agents: Phosphorous and sulphur compounds.
Biostabilisers: OBPA, (10,10-oxybisphenoxarsine), 8-quinolinolate, N-(trichloromethylthio)phthalimide, zinc pyrithione, etc.
Antioxidants/UV Absorbers: Benzotriazoles, zinc oxide, titanium dioxide etc.

Entre los aditivos de PVC, los compuestos mayoritarios en PVC flexible son los plastificantes. En términos de uso, sobre el 30% de la producción total en Europa de resina de PVC se utiliza para productos flexibles (Organización PVC, http://www.pvc.org/en/p/what-is-pvc). Por lo tanto, con el fin de distinguir entre

PVC rígido y flexible, la IUPAC ha adoptado la nomenclatura PVC-P, para plastificado de PVC y PVC-U para el polímero no plastificado (Leadbitter *et al.*, 1994; Kricheldorf *et al.*, 2004; Wilson, 1995). Los plastificantes, que se define como "sustancias incorporadas en un material para aumentar su flexibilidad, suavidad, distensibilidad o capacidad de trabajo", son típicamente líquidos orgánicos oleosos de alto punto de ebullición (Wilson, 1995).

Debido a la temperatura de transición vítrea (Tg) del cloruro de polivinilo de 83ºC, el polímero de PVC hace que se comporte como un sólido frágil a temperatura ambiente. La adición de una pequeña cantidad de plastificante al PVC puede reducir la Tg 40ºC grados), haciendo el PVC flexible (Wilkes *et al.*, 2005), y así utilizable para la fabricación de una amplia gama de productos. Sin embargo, mediante la adición de plastificantes, no sólo disminuye la Tg, sino que también disminuyen la cristalinidad del polímero de PVC, la resistencia a la tracción y la resistencia química, que son claramente inconvenientes para su uso (Chanda y Roy, 2006). Además, algunas propiedades del PVC, tales como dureza, resistencia a la tracción, alargamiento a la rotura, flexibilidad, módulo de baja temperatura y fragilidad, están influenciados por el nivel y el tipo de plastificantes (Wilkes et al., 2005). Esto significa, que los cambios en la proporción y naturaleza del plastificante en la composición de PVC afectan al comportamiento físico y mecánico del polímero.

Desde un punto de vista físico, el PVC plastificado tiene la morfología clásica de un TPE (elastómero termoplástico) y tiene enlaces cruzados físicamente estables y fundibles que consisten en cristales de PVC (Figura 7, Wilkes *et al.*, 2005), que sobreviven en presencia de plastificante hasta temperaturas de aproximadamente 160ºC y superiores. En el PVC, los plastificantes no están ligados químicamente al polímero de PVC, pero se encuentran incrustados entre las cadenas de polímero y se unen a la red del PVC por fuerzas intermoleculares.

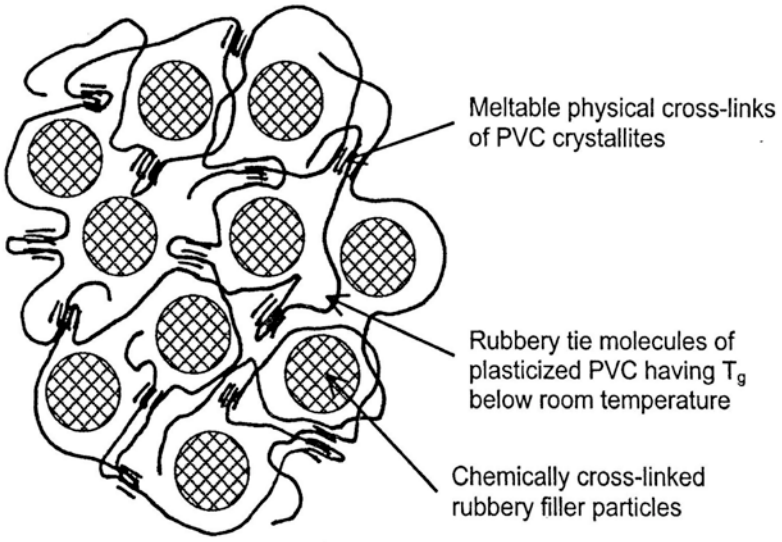


Figura 7: Morfología del PVC plastificado

La posición del átomo de cloro en la cadena de hidrocarburo conduce a fuerzas de valencia secundaria altamente polares que permiten a los plastificantes actuar como enlace en el polímero. A pesar de que existe una alta diversidad de plastificantes que se puede agregar a polímero de PVC, la mayoría pertenece a la familia de los ésteres de ftalato. Entre estos, los ftalatos preparados a partir de alcoholes con alrededor de ocho átomos de carbono constituyen alrededor del 75% de los plastificantes utilizados (Brydson, 1999). Comercialmente, los plastificantes más comunes utilizados para PVC son: ftalato de diisononilo (DINP), ftalato de diisodecilo (DIDP) y ftalato de di-2-etilhexilo (DEHP, a veces también referido como DOP). Además, el di-iso-octil ftalato (DIOP), el ftalato de di- 2-etilhexilo (DEHP o DOP) y el éster de ftalato de oxo-alcohol C_7-C_9, también conocido de manera extraoficial como dialil ftalato (DAP), se han utilizado generalmente por razones económicas (Brydson, 1999).

Los plastificantes diferentes de los ftalatos son, por ejemplo: trimelitatos como tri (2-etilhexil) trimetilato (TOTM) o tri (isononilo) trimetilato (TINTM); poliésteres, formados por la esterificación de glicol de propileno o butileno con ácidos dibásicos

alifáticos; adipatos, tales como di (2-etilhexil) adipato (DOA) o di (isononilo) adipato (DINA); fosfatos como tri (2-etilhexil) fosfato (TOF) o fosfato de tricresilo (TCP) y epóxidos, como "octyl epoxy tallate" (OET) o aceite de soja epoxidado (ESO). Por otra parte, otros tipos de plastificante son los llamados "como ftalato", que corresponden a los compuestos como ésteres, benzoatos, citratos etc. (Tabla 5, Wilkes *et al.*, 2005).

Además de plastificantes, los extensores son otra clase de aditivos que se puede utilizar en combinación con los plastificantes, a pesar de su muy baja compatibilidad (Chanda y Roy 1998). Los extendedores típicos son las ceras de parafina clorados, fracciones parafínicas líquidos cloradas y extractos de aceite (Brydson, 1999).

Tabla 5. Familia de plastificantes y sus propiedades.

Family	**General purpose**	**Performance plasticizer**			**Specialty plasticizers**		
		Strong solvent	**Low temp.**	**Low volatility**	**Low diffusion**	**Stability**	**Flame resistance**
Phthalates	X	√	√	√	√		√
Trimellitates			√	X	√		
Aliphatic dibasic esters			X				
Polyesters				X	X		
Epoxides			√	√		X	
Phosphates		√	√				X
Extenders	X						

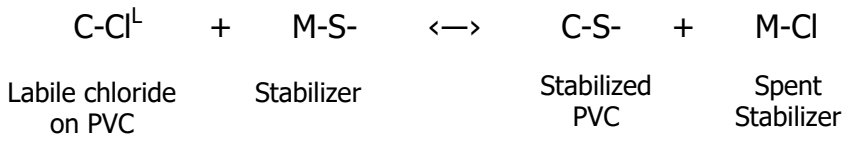
X = Primary performance function

√ = Secondary performance function

Los lubricantes son los aditivos destinados a mejorar el flujo del PVC fundido (Chanda y Roy, 1998). Principalmente se pueden clasificar como lubricantes internos o externos en base a su compatibilidad con el PVC. Los lubricantes internos son aquellos con una compatibilidad moderada con el PVC, tales como alcoholes grasos, ácidos grasos, ésteres grasos y amidas grasas, ceras, mientras que los no polares, tales como la parafina y el polietileno o las ceras son incompatibles con el PVC y se

denominan como "lubricantes externos" (Wilkes *et al.*, 2005). La función principal de lubricantes externos es evitar la adherencia del compuesto al equipo de procesamiento (Chanda y Roy, 1998).

Por otro lado, cuando el PVC se calienta a 170-180ºC, se eliminan átomos de cloro e hidrógeno de las cadenas, liberando cloruro de hidrógeno, lo que provoca la degradación del PVC. Como durante la fabricación de PVC (moldeo y extrusión) se alcanzan estas altas temperaturas, se añaden **estabilizadores** para evitar la pérdida de HCl durante este proceso de fabricación. La degradación térmica de las moléculas de PVC comienza en las cadenas que tienen defectos y se produce hasta que una molécula de estabilizador activo está cerca del sitio del que se desprenden los lábiles átomos de cloro del PVC por el siguiente mecanismo (Wilkes *et al.*, 2005):



La clase más importante de los **estabilizadores** son compuestos de plomo, que forman cloruro de plomo en la reacción con el cloruro de hidrógeno desprendido durante la descomposición. El carbonato de plomo (blanco de plomo), que tiene un coste bajo, es el más comúnmente utilizado (Chanda y Roy, 1998), aunque puede liberar CO_2 y aumentar la porosidad en el producto. Por ello, se ha sustituido por otros compuestos de plomo como el sulfato de plomo tribásico o el ftalato de plomo dibásico (Chanda y Roy, 2006). Sin embargo, debido a su toxicidad, los estabilizadores a base de plomo actualmente están siendo reemplazados por compuestos de cadmio, bario, epóxidos o compuestos organoestánicos (Brydson, 1999).

Otro tipo de aditivos añadidos al PVC con el fin de prevenir de la degradación debido al calor y la luz son los absorbentes **antioxidantes** y **ultra-violeta** (UV). Los antioxidantes primarios, típicamente derivados de fenol, son esencialmente

agentes neutralizantes de los radicales libres, al interrumpir el progreso de la degradación oxidativa, que se cree generalmente que se lleva a cabo a través de un mecanismo de radicales libres, y así mejorar la estabilidad al calor de los compuestos de PVC, así como la estabilidad a la luz (Titow, 1984). Los absorbentes de UV-violeta evitan la degradación del PVC absorbiendo la luz en el intervalo de 290-400 nm y pueden ser tanto de carácter inorgánico y orgánico. Como ejemplo de los absorbentes de UV inorgánicos comunes son el dióxido de titanio o el óxido de zinc, que refleja principalmente y dispersan la radiación UV entrante, la radiación IR o la radiación visible. Los compuestos orgánicos absorbentes de UV añadidos al PVC son las benzofenonas modificadas, benzotriazol y derivados cianoacrilatos, que absorben la radiación UV incidente evitando su acción perjudicial sobre el material de PVC (Titow, 1984).

Los materiales de relleno se definen en la industria del PVC como de partículas inertes sólidos que se incorporan en formulaciones con el fin de inducir el endurecimiento, la rigidez o la reducción del coste (Wilkes *et al.*, 2005). Se utilizan diversos carbonatos de calcio (Chanda y Roy, 1998) y en las formulaciones de PVC flexibles, los plastificantes pueden mejorar la capacidad de PVC para aceptar un alto contenido de los materiales de relleno (Menges, 1996).

Los modificadores de impacto se utilizan generalmente como aditivo en el PVC no plastificado con el fin de superar los problemas de procesamiento y la alta fragilidad de los productos terminados. Estos aditivos son generalmente semi-compatibles con la estructura del polímero y, a menudo, de naturaleza algo gomosa (Chanda y Roy, 1998). Los modificadores de impacto típicos son: acrilonitrilo-butadieno-estireno terpolímero (ABS), termopolymer metacrilato-butadieno-estireno (MBS), polietileno clorado (CPE), copolímero de etileno-acetato de vinilo (EVA) y polimetacrilato acrilato copolímero (ACE) (Leadbitter *et al.*, 1994).

11.2.4. Degradación

El PVC es hoy utilizado principalmente para aplicaciones de larga duración gracias a su excelente relación precio/rendimiento y su excepcional resistencia química y ambiental (Menges, 1996). La presencia de cloro en el polímero proporciona PVC con capacidad ignífuga, aunque esta propiedad se reduce por la presencia de plastificantes (Brydson, 1999), que también reducen las propiedades de aislamiento de PVC, resistencia al impacto y atributos a prueba de agua (Chanda y Roy, 1998). Los enlaces carbono-cloro en el PVC se pueden disociar más fácilmente que los de carbono-hidrógeno, debido a su baja energía de enlace y la dislocación carga eléctrica que facilita la reacción química (Wypych, 2008).

El polímero de PVC es resistente a los ácidos, bases y a la mayoría de los hidrocarburos, aunque disolventes polares pueden extraer plastificante cuando éste forma parte del PVC. Un resumen de la resistencia y principales características químicas tanto del PVC plastificado como del no plastificado se muestra en la Tabla 6 (Titow , 1984) .

Tabla 6: Características generales del PVC a temperatura ambiente.

Reagents	**Rigid PVC**		**Plasticised PVC**	
	General resistance ratinga[a]	**Remarks**	**General resistance rating[a]**	**Remarks**
Inorganic acids:				
Dilute	S	No attack up to 60°C, but max. allowable design stress should be lowered	S	No significant attack up to 20°C; plasticisers and some fillers may be affected at higher temperatures
Concentrated	S		M	Plasticiser and some fillers may be affected
Oxidising (concentrated)	M	Attacked above 20°C; max. allowed design stress should be reduced substantially	U	Short-term contact may be acceptable in some cases
Organic acids	M		M	
Alkalis:				
Dilute	S	No attack up to 60°C; allowable design stress should be substantially reduced	S	Some plasticisers and fillers may be affected
Concentrated	M		M	

Oxidising agents	S		Allowable design stresses should be substantially reduced	S	Some fillers may be affected
Reducing agents	S	}	No attack up to 60°C	S	} No attack up to 60°C
Detergent solutions	S			S	
Inorganic salt solution	S			S	
Halogens:					
Chlorine	M		Little attack in the absence of moisture	U	
Bromine	U			U	
Fluorine	U			U	
Iodine	U			U	
Aliphatic alcohols	S		Allowable design stresses should be substantially reduced	M	
Water	S		Some softening possible at elevated temperatures	S	Softening, and some effects on certain fillers at elevated tamperatures
Aliphatic hydrocarbons	S			M	Extraction of plasticisers and some effects on other components possible
Aromatic hydrocarbons	U			U	
Chlorinated hydrocarbons	U			U	
Esters	U			U	
Ethers	U			U	
Ketones	U			U	
Aldehydes	M			M	
Amines	M			M	
Liquid fuels	S-M			M-U	
Turpentine	U			U	
Oils:					
Mineral	S			M-U	
Vegetable and animal	S			M-U	
Fats	S			M-U	

[a]Rating key: S = Satisfactory; M = Moderate (dependent on formulation and conditions); U = Unsatisfactory.

En general, la resistencia a la degradación PVC depende en gran medida del agente de degradación, mostrando una alta vulnerabilidad a cualquier forma de oxidación, mientras que no se ve afectada por hidrólisis u ozonolisis (Tabla 7, Grattan, 1993).

Durante el procesamiento, el almacenamiento y la utilización del PVC, éste puede degradarse cuando se expone a altas temperaturas, altas tensiones mecánicas o a luz ultravioleta en presencia de oxígeno. Sin embargo, la inestabilidad a la luz y a la temperatura del poli (cloruro de vinilo) es causada por anormalidades estructurales (defectos) que están presentes, en diverso grado, en los polímeros disponibles comercialmente.

Tabla 7. Resistencia del PVC a la degradación

Thermal Deterioration of PVC (Maximum Use Temperature for 2. 0 mm film thickness)	**Susceptibility of Unstabilized PVC Polymers to Degradation**				
50ºC	**Thermal Oxidation**	**Photo-oxidation Weathering**	**Ozone**	**Hydrolysis**	**Oxidation**
	Very Poor	Poor	Excellent	Excellent	Poor

Por lo tanto, los dos principales procesos en cadena pueden ocurrir simultáneamente durante la degradación fotolítica y térmica del poli (cloruro de vinilo) (Rabek, 1995):

1- Deshidrocloración en cadena,

2- Procesos de oxidación en cadena.

En el primer proceso, la degradación del polímero se produce por eliminación sucesiva de cloruro de hidrógeno (HCl), llamado deshidrocloración (mecanismo descrito en la Figura 8) (Rabek, 1996). Una vez se inicia la deshidrocloración, la progresiva eliminación de átomos de cloro y de hidrógeno adjacentes puede ocurrir a lo largo de la cadena del polímero, formando estructuras de cloruro de alilo, que es catalizada por la liberación de HCl (Leadbitter *et al.*, 1994). La liberación de HCl produce la formación de polienos (-CH=CH-)n, siendo n un número entre 2 y 13 (Rabek, 1996), que tienden a absorber luz visible produciendo amarilleamiento del polímero hasta finalmente oscurecerlo (Lister y Renshaw, 2004). Puesto que los principales plastificantes en los compuestos de PVC son ésteres, la producción de HCl como consecuencia del proceso de deshidrocloración puede afectar a su estabilidad debido a hidrólisis ácida, lo que dependerá del tipo de plastificante (Wypych, 2013).

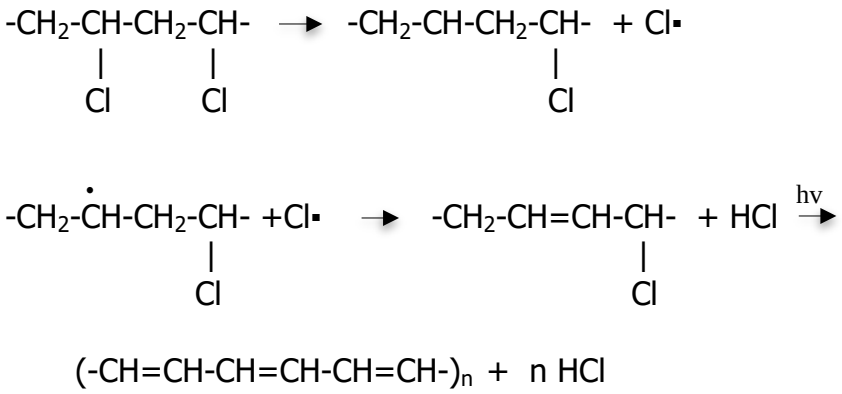


Figura 8: Dehidroclorinación y formación del doble enlace.

El poli (cloruro de vinilo) contiene sólo enlaces C-C, C-H y C-Cl, por lo que no absorbe radiación de longitudes de onda mayores de 190 nm, debiéndose su cambio de color a a la formación de las estructuras de poliénicas. Sin embargo, a pesar del cambio de color, los polienos forman una capa protectora superficial que impide una mayor degradación de las zonas internas, debido a su fuerte absorción de la luz UV (Rabek , 1995).

Tras la deshidrocloración se produce la escisión y entrecruzamiento de la cadena polimérica (von Hans Zweifel *et al.*, 2009), lo que conduce al debilitamiento del polímero envejecido (Owen, 1984), al deterioro de las propiedades mecánicas y a una disminución de la resistencia química (Pauwels, 2004). El segundo proceso mencionado anteriormente es la oxidación en cadena, que conduce a la formación de grupos hidroperóxidos, peróxidos de dialquilo y carbonilos, junto con las reacciones de entrecruzamiento y escisión de la cadena polimérica (Rabek, 1995; Rabek, 1996). Además de la degradación del polímero, otra forma importante de degradación de PVC plastificado es la pérdida y migración de plastificante. La forma más común de pérdida de plastificante es la evaporación de PVC en el aire circundante (debido a su volatilidad). Puesto que no hay unión química entre el polímero y el plastificante, la evaporación se produce de forma continua incluso a bajas temperaturas y es controlada por la difusión y evaporacion del plastificante desde la superficie (Wilson, 1995).

Ha sido reportado, que tanto la pérdida de plastificante como su migración se pueden producir en objetos de PVC plastificado en museos. Las consecuencias de estas formas de degradación es la formación de superficies pegajosas, debido a la migración del plastificante a la superficie, así como el aumento de fragilidad y rigidez, debido a la pérdida de plastificante (Quye y Williamson, 1999; Shashoua, 2001; Shashoua, 2008; Morgan, 1994). Además del plastificante, otros aditivos presentes en el polímero PVC y añadidos durante el proceso de fabricación pueden migrar a la superficie, que puede observarse como partículas depositadas en la superficie del objeto (Figura 9). Así mismo, los aditivos de PVC pueden también deteriorarse o reaccionar con sustancias del entorno, causando el deterioro del polímero de PVC en el que están inmersos. Los estabilizantes de plomo, por ejemplo, pueden ennegrecerse si son expuestos a sulfuro de hidrógeno (Morgan , 1994).

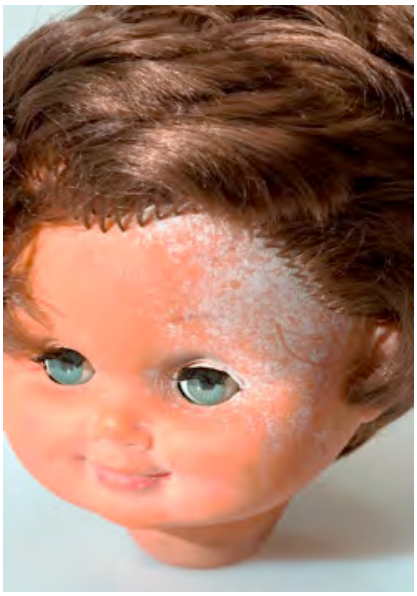


Figura 9. Cabeza de muñeca de PCV plastificado sufriendo de la migración de aditivos hacia la superficie.

Debido a la su alta volatilidad y a sus características químicas, los plastificantes no sólo migran fácilmente desde el interior del polímero de PVC a la superficie y se evaporan, sino que también son fácilmente extraídos por líquidos orgánicos y sólidos en contacto con ellos. El agua reduce la compatibilidad de los plastificantes con el polímero de PVC, así como proporciona un mecanismo para la dispersión del plastificante cuando contiene tensioactivos, haciendo que éste llegue a

la superficie y pueda ser extraído (Wilson, 1995). Así mismo, los plastificantes pueden migrar fácilmente a sólidos o polímeros adyacentes, lo que supone un problema cuando los plastificantes están en contacto con otros plásticos, tales como material de embalaje o dispositivos médicos (Bernard *et al.*, 2015). La manipulación de PVC envejecido cerca de alimentos puede causar graves problemas de salud debido a la migración del plastificante. En museos, se ha observado el deterioro de cámaras fotográficas compuestas de poliestireno en contacto con correas PVC, ya que el plastificantes actúa como disolvente del poliestireno (Morgan, 1994).

Además de su migración del PVC, los plastificantes son propensos a la fotodegradación. En el caso de los ésteres de ftalato (principales plastificantes de PVC), la fotodegradación da lugar a alquenos, alcoholes, anhídrido de ácido ftálico, ésteres de 2-formil ácido benzoico y ésteres de ácido benzoico, como principales productos de degradación, producida por la escisión simultánea de los dos grupos éster y de los enlaces C-C de un grupo carbonilo conectado al anillo aromático (Balabanovich y Schnabel , 1998).

Por otra parte, la degradación térmica de los ésteres de ácido ftálico da lugar a su fragmentación en monoésteres de ácido ftalato y alcoholes. A continuación, el ácido ftálico se convierte en anhídrido ftálico a 230º, mientras que los alcoholes se convierten en agua y un resto hidrocarburo insaturado (Figura 10 , Wypych, 2013) a una determinada temperatura de ebullición dependiendo del peso molecular y la ramificación del alcohol.

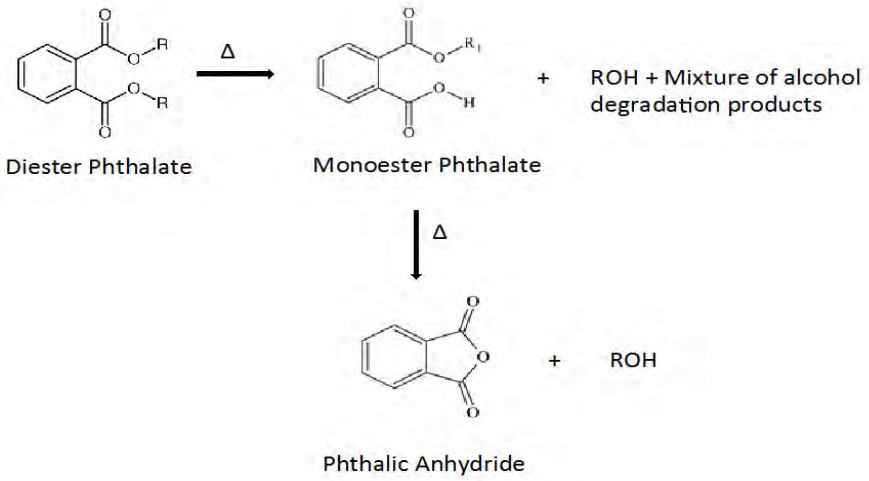


Figura 10. Degradación térmica de los esteres ftalicos.

11.3. Conservación de los objetos de plástico.

En museos, los plásticos pueden encontrarse como objetos artísticos en sí mismos (Figura 11), formando parte de materiales de embalaje o de exposición, o como substancias utilizadas en tratamientos de restauración, tales como adhesivos, materiales de refuerzo etc. (Horie, 1994; García *et al.*, 2009) . Dentro de los plásticos utilizados en los objetos artísticos, se puede encontrar una alta diversidad (Blank, 1990; Williams *et al.*, 1998; Shashoua, 2001; Quye y Williamson, 1999), tales como acrílicos, policarbonatos, acetato de celulosa, nitrato de celulosa, nylon (poliamida), polietileno, polipropileno, fenol formaldehído, urea formaldehído, melamina, poliéster, poliolefina , poliestireno, poliuretano, poli (cloruro de vinilo), caucho , etc.

Figura 11. Anders Krisár: "Cuirass" (2005). Fotografía cortesía del artista.

Dentro de las colecciones de arte, existen numerosos ejemplos de artistas conocidos que hicieron un amplio uso de materiales plásticos en sus obras. Por ejemplo, PVC plastificado fue utilizado por el artista belga Panamarenko (1940), así como Naum Gabo (1890-1977) hizo uso de plexiglás (nombre comercial de polimetacrilato de metilo, PMMA) y Nylon (familia poliamida alifática) en sus obras. Otros artistas han empleado espumas, como Dubuffet (1901-1985), quien aplicó poliestireno expandido (EPS) en sus esculturas, o Pistoletto, que utilizó espuma de poliuretano duro es su obra " Scultura Nera" en 1983 (van Oosten *et al.*, 2002).

Desde una perspectiva de la conservación de arte, los plásticos son compuestos complejos que han comenzado a estudiarse recientemente, en comparación con los materiales tradicionales. Así mismo, el interés en su conservación se ha incrementado de manera significativa en los últimos años dentro la comunidad científica (Keneghan, 2005). Conferencias especializadas (Grattan, 1993) y simposios internacionales se han celebrado sobre este tema (Keneghan y Egan, 2008) con el propósito de concienciar a los conservadores de la presencia de materiales plásticos en las colecciones y las crecientes dificultades que rodean su conservación.

A diferencia de obras de arte tradicionales, muchos materiales plásticos se degradan fácilmente, lo que depende de la composición química y las características físicas del polímero en particular. Por tanto, deben definirse acciones específicas con el fin de

mitigar la degradación de los plásticos. A su vez, la amplia gama de formulaciones químicas dentro de los plásticos conlleva a muchas dificultades en la selección de métodos de conservación y limpieza, (Blank, 1990), lo que ha incrementado recientemente la investigación en plásticos (Madden y Learner, 2014)

Estudios dedicados a la investigación y conservación de estos materiales particulares han sido desarrollados por investigadores especializados, con el propósito de comprender la composición y los procesos de degradación de los objetos plásticos (Shashoua, 2001; van Oosten *et al.*, 2002; Chércoles Asensio *et al.*, 2009), aumentando su longevidad en museos y colecciones de arte.

Considerando la definición proporcionada por Salvador Muñoz Viñas, conservación es: "Cualquier acción tomada con el fin de la determinación de la naturaleza o las propiedades de los materiales en cualquier tipo de patrimonio cultural o en su alojamiento, cualquier manipulación o tratamiento, cualquier acción llevada con el fin de comprender y controlar el deterioro y cualquier acción tomada para el final de mejorar la condición de esos patrimonios" (Muñoz Viñas, 2005). Por tanto, es evidente que los materiales plásticos tienen que ser considerados parte de nuestro patrimonio cultural, pudiendo ser sometidos a tratamientos de conservación.

Con el fin de conservar los objetos realizados en plástico de los museos y colecciones de arte, uno de los pasos más importantes es la identificación del material plástico (Blank, 1990; Williams *et al.*, 199). Por ello, cuanto más precisa es la determinación de la composición química, más preciso será el tratamiento de conservación. Debido a la complejidad de los materiales plásticos y de las técnicas utilizadas para identificar su composición química, la determinación de los plásticos que componen los objetos expuestos en museos y galerías de arte no siempre es posible que se realice in situ. Por esta razón, se han hecho esfuerzos por parte de los investigadores, con el fin de proporcionar a los conservadores herramientas simples para determinar la naturaleza de los objetos de plástico.

El primer paso en la identificación de los polímeros es un examen visual. Mientras la apariencia de la muestra puede indicar si se trata de un polímero en bruto o un elemento compuesto y procesado, otras características físicas como su forma, tacto, olor, color, transparencia, opacidad, suavidad, rigidez, fragilidad o textura de superficie, pueden ser importantes en el proceso de identificación del polímero. El poliestireno, por ejemplo, es un polímero de uso general transparente y quebradizo, que produce un tintineo metálico característico cuando los objetos realizados mediante moldeo de este material se dejan caer o son golpeados (Shashoua, 2001). A su vez, el reconocimiento visual de las marcas de moldeo producidos durante el proceso de fabricación puede ser útil en la identificación de muchos objetos de plástico en museos, ya que ciertos procesos dejan marcas en el producto terminado y ciertos plásticos sólo se utilizan en ciertos procesos.

A parte de la identificación visual, otras herramientas simples y útiles utilizadas a menudo por los conservadores para identificar los materiales de plástico son la detección de nombres comerciales en el objeto (la baquelita, por ejemplo, es el nombre comercial dado originalmente a la resina producida a partir de fenol y formaldehído), el estudio de las propiedades físicas (apariencia, flexibilidad, etc.) (Coxon, 1993) o la realización de tests químicos, tales como: el "burn test" (o quemado de una muestra), medición del pH, pruebas de solubilidad, pruebas de densidad y "spot tests" (pruebas químicas simples con proporciones mínimas de muestra) (Coxon, 1993; Williams, 2000)

Técnicas químicas más complejas también se han utilizado en Conservación para el análisis y la identificación de los materiales plásticos y sus aditivos (Quye y Williamson, 1999). Técnicas espectroscópicas, tales como espectroscopía de infrarrojos (IR) o espectroscopía Raman, o cromatográficas, como la cromatografía de gases acoplada a detección de masas (GC-MS), se han aplicado con éxito para la identificación de polímeros y aditivos en plásticos, por lo que su uso también ha sido aplicado en conservación (Quye y Williamson, 1999; Seidel, 2008; Koenig, 2008; Shashoua, 2008; Keneghan, 2005; Keneghan y Egan, 2008; Derrick *et al.*, 1999).

Otras técnicas más recientes como, por ejemplo, la espectroscopía de Tera-hertz (THz) también se han utilizado con fines de conservación de polímeros (Pastorelli *et al.*, 2012). Todas estas técnicas de análisis serán discutidas en detalle en la sección de técnicas analíticas.

Como se ha explicado anteriormente, además de la correcta identificación de los polímeros que forman los objetos realizados en plástico en los museos, otro problema importante es la degradación de los mismos. Los problemas de degradación de los materiales plásticos han sido objeto en los últimos años de varias investigaciones realizadas en museos y colecciones de arte (Shashoua, 2001, Morgan, 1991). Estos procesos de degradación pueden ser extremadamente complejos y diversos, ya que dependen del tipo de polímero que se aborde. Cada tipo de material plástico tiene una naturaleza química particular que hace que sea susceptible en un modo único a los agentes de degradación. Por tanto, aun sometidos a las mismas condiciones ambientales, cada tipo de plástico reaccionará de una manera inherente a su naturaleza química y física. Así mismo, algunos plásticos pueden sufrir degradación química, mientras que otros pueden experimentar una degradación física o biológica, pudiendo cambiar no sólo la composición química del material, sino también las características físicas o la apariencia de los objetos (Williams *et al.*, 1998). El PVC plastificado, por ejemplo, puede sufrir procesos de degradación cuando se somete a ciertas condiciones de luz y temperatura. Estos procesos de degradación se han identificado en objetos hechos de PVC plastificado que forman parte de colecciones de arte (Shashoua, 2001), suponiendo un riesgo para su conservación y preservación. Con el fin de evitar una mayor degradación del material, la identificación de las primeras etapas de la degradación es fundamental en los museos y colecciones de arte, mediante el examen y el control del estado de conservación de los objetos de plástico.

La degradación en plásticos puede ocurrir debido a varios factores como la humedad, la temperatura, los contaminantes, el oxígeno, la radiación UV o fuerzas físicas que afectan a los materiales plásticos. Las consecuencias para los mismos son

muy diversas y pueden incluir (Shashoua, 2008; Williams *et al.*, 1998; Morgan, 1991; Cheng, 2002; Williams, 1997):

- Cambios en el color debido a la formación de grupos cromóforos (dobles enlaces conjugados etc.);
- Pérdida de fortaleza y aumento de la fragilidad causados por la pérdida de plastificante y aditivos, o modificaciones de solubilidad debido al entrecruzamiento de las cadenas de polímero;
- Formación de superficies pegajosas debido a la migración de aditivos y plastificante a la superficie, floraciones en el objeto;
- Atracción de partículas abrasivas o higroscópicas debido al aumento de electricidad estática, etc.

En el caso del PVC, las propiedades ópticas y superficiales pueden ser modificadas severamente por los procesos de oxidación y de deshidrocloración que se inician en la capa superior del material (Owen, 1984). Estas alteraciones pueden detectarme por el color amarillo que adquiere la superficie debido a la formación de dobles enlaces conjugados. También el blanqueo del PVC con el tiempo se produce como consecuencia de los procesos de oxidación (Wilkes *et al.*, 2005). A su vez, el PVC plastificado puede sufrir la pérdida de aditivos, como plastificantes y lubricantes, que en ocasiones son detectados visualmente sobre la superficie de PVC, indicando la degradación del material (Shashoua, 2008).

Con el fin de preservar las obras de arte realizadas en plástico que se encuentran presentes en museos, la comunidad científica ha tratado de buscar directrices generales que ayuden a los conservadores y restauradores a preservar estos materiales particulares. Algunas de las recomendaciones que pueden encontrarse en la literatura (Quye y Williamson, 1999; Blank, 1990; Williams *et al.*, 1998; Morgan, 1991) son por ejemplo:

- La exposición mínima a la luz a fin de evitar la foto-degradación debe ser de 50 a 100 lux;

- La humedad relativa debe ser estable y controlada (en valor igual o inferior al 55%, dependiendo de la susceptibilidad de cada material plástico), con el fin de evitar hidrólisis;
- La temperatura debe ser estable y controlada (entre 15 y 20 grados Celsius) a fin de evitar efectos de degradación térmica;
- Las salas de exposición y almacenamiento deben estar ventilado para evitar daños que los vapores de algunos plásticos puedan ejercer sobre otros plásticos próximos;
- Control de la limpieza para evitar la degradación causada por los contaminantes;
- Evitar el contacto entre plásticos para prevenir la migración de los aditivos de un plástico a otro;

Por último, pero no menos importante, es de destacar que en el campo de la conservación es de gran importancia no sólo la preservación de objetos plásticos, sino también la salud de los conservadores que tratan con materiales plásticos en el ambiente del museo. Los vapores liberados por los plásticos degradados, así como la migración de aditivos a la superficie de los objetos pueden llegar a ser tóxicos para las personas que trabajan con estos objetos. Por ello, varios autores han proporcionado directrices para la práctica y el manejo seguro de los plásticos en museos con el fin de evitar las consecuencias negativas para la salud de los restauradores, conservadores y profesionales directamente expuesto o en contacto con plásticos degradados (Tsang, 2010).

Resumiendo todos los aspectos antes mencionados relacionados con la conservación de materiales plásticos, se puede afirmar que mediante "la aplicación del creciente conocimiento físico y químico de los plásticos, es posible desarrollar un plan de conservación y una estrategia de gestión del arte moderno que contiene estos materiales" (van Oosten *et al.*, 2002). En este contexto, los métodos para la limpieza de los objetos plásticos pueden ser considerados como los menos generalizables, debiendo generar métodos a medida para cada tipo de polímero.

11.3.1. Limpieza de objetos plásticos.

Las primeras definiciones de limpieza y pátina relacionadas con las obras de arte fueron dadas por el artista toscano Filippo Baldinucci a finales del siglo XVII. En su "diccionario Italiano" dice, que el término limpiar ("pulire") no significa sólo eliminar la suciedad y las manchas, sino también "pulir, principalmente el mármol y el metal". La " patena" (pátina) que puede eliminarse mediante esta acción se define como un cambio visual del tiempo en el objeto, que puede favorecer la obra, apuntando claramente al conflicto central de toda acción de restauración (Baldinucci de 1681). Durante décadas, la limpieza de objetos de arte ha sido objeto de discusión en los manuales de conservación y restauración, por lo que muchas teorías y ensayos han relacionado los conceptos principales de "la limpieza de obras de arte" en términos de la teoría de la conservación (Brandi, 1977; Baldini, 1997). Desde un punto de vista lógico la primera pregunta a considerar debería ser: "¿Por qué limpiar un objeto de arte?"

La primera y más intuitiva respuesta a esta pregunta es asumir que la acción de limpieza mejora la apariencia y significado del objeto, recuperando el propósito inicial del artista, al mostrar un objeto cercano de la original. Sin embargo, ésta es también la respuesta más polémica, que ha dado lugar a largas discusiones acerca de la intervención estética por parte del restaurador y a las consecuencias posteriores para el objeto de arte (Hedley, 1986). Durante décadas, la limpieza de obras de arte famosas ha sido objeto de debate, dando lugar a una fuerte división entre los que apoyan los tratamientos utilizados y los que los critican (Keck, 1984). A lo largo de la historia de la conservación, muchos autores han alzado sus voces para criticar limpiezas excesivas y políticas de limpieza inadecuadas. Umberto Baldini, en su "Teoria del restauro e Unità di Metodología" (Baldini, 1978), recomienda tratamientos de limpieza equilibradas que respeten la superficie original y el paso del tiempo en el material, así como señala la importancia que tiene la preservación de la historicidad del objeto. Por tanto, limpiezas excesivas deben evitarse o, al menos, reevaluarse con el fin de evitar la eliminación de las características inherentes a la obra de arte.

Por otra parte, desde un punto de vista más teórico, Cesari Brandi afirma en su conocida "Teoria del Restauro" que cualquier tratamiento de restauración debe centrarse en la recuperación potencial de la obra, pero respetando los signos del paso del tiempo en la misma (Brandi, 1977). Esta declaración hace referencia a todos los tratamientos de restauración, siendo la limpieza una parte fundamental.

En las últimas décadas, ejemplos famosos de limpiezas controvertidas incluyen la limpieza de la "Capilla Sixtina" de Miguel Ángel, la "Ultima Cena" de Leonardo Da Vinci, así como el tratamiento de limpieza excesivo y no autorizado de los "Mármoles del Partenón" (1937-38) en el Museo Británico de Londres, el cual ha sido ampliamente documentado (Jenkins, 2001)

A pesar de que los plásticos son materiales relativamente recientes, en la literatura pueden encontrarse recomendaciones sobre su limpieza en el ámbito del museo, siguiendo las teorías de conservación generales comentadas anteriormente. En 1994, John Morgan afirmó en referencia a los métodos de limpieza de plásticos que: "los procedimientos de limpieza llevan consigo un riesgo de daño asociado, por tanto los métodos empleados deben ser cuidadosamente considerados y controlados" (Morgan, 1991). Desde entonces, otros autores e instituciones han investigado activamente tratamientos de conservación para plásticos (Quye y Williamson, 1999; Shashoua, 2001; Williams, 2000; Grattan, 1993; van Oosten *et al.*, 2002; Keneghan, 2005; Keneghan y Egan, 2008). Esta parte se desarrollara con mayor detalle en la siguiente sección de este capítulo.

Una segunda respuesta a la pregunta anteriormente planteada está relacionada con el efecto positivo de los tratamientos de limpieza en relación a la conservación de obras de arte. En primer lugar, es aceptado de forma general que la eliminación de la suciedad de las superficies de los objetos reduce el riesgo potencial de deterioro. Esto se debe principalmente al hecho de que el daño mecánico causado por sustancias erosivas de sedimentación en las superficies de los objetos de plástico, es evitado mediante la eliminación de estas partículas nocivas. Además, los

tratamientos de limpieza pueden reducir la tasa de deterioro químico mediante la eliminación de la suciedad, ya que las partículas de polvo, escamas de piel o grasa, entre otras sustancias, pueden favorecer que el agua y contaminantes ácidos se depositen en las superficies de los objetos. En el caso particular de materiales realizados en plástico, la limpieza se ha identificado como un potencial "elemento conservación" no sólo por a la eliminación de contaminantes y partículas erosivas, sino también porque los productos de degradación aceleran el deterioro, siendo esta degradación iniciada en muchos casos por contaminantes depositados en la superficie del objeto, tales como oxígeno o iones de metales (Morgan, 1991).

Considerando los argumentos anteriormente expuestos, parece claro que los procesos de limpieza son un importante paso adelante en la futura preservación del patrimonio cultural. Sin embargo, los "efectos secundarios" de los procesos de limpieza también deben tenerse en cuenta cuando se limpia un objeto artístico. Al igual que cualquier otro tratamiento de limpieza en conservación, la limpieza de un objeto de plástico debe garantizar que ningún daño inmediato o de largo plazo se produce como consecuencia de dicho tratamiento. Esto significa que la eliminación de la suciedad debe ser abordada en un modo que garantice el mínimo riesgo para el objeto de plástico. A diferencia de los métodos de limpieza empleados en otros materiales tradicionales, tales como pintura o piedra, los métodos de limpieza para los compuestos plásticos deben hacer frente a una amplia diversidad química. Este hecho aumenta la dificultad de encontrar métodos de limpieza seguros que puedan ser aplicados a todos los tipos de materiales plásticos. Por otro lado, los materiales plásticos son altamente susceptibles a la degradación y, por tanto, a menudo se encuentra en condiciones de degradación en museos y colecciones de arte (Shashoua, 2001). Este hecho requiere que los conservadores busquen tratamientos de limpieza más específicos que salvaguarden objetos realizados en plástico, independientemente de su composición química o de su estado de conservación (degradado o no degradado).

11.3.2. Métodos de limpieza.

Con el fin de encontrar un método de limpieza exitoso, el primer paso en la metodología es la identificación y caracterización del material que va a ser limpiado, así como de las sustancias que van a ser eliminadas. En cuanto a las partículas a eliminar, éstas pueden provenir de cualquiera de los diferentes ambientes en los que el objeto ha sido expuesto durante su vida útil, por lo que pueden incluir una amplia gama de compuestos. El uso del objeto antes de ser parte de la colección de arte puede ser, por ejemplo, la causa de acumulación de huellas dactilares y grasa sobre la superficie del objeto. Asimismo, partículas de polvo, células muertas de la piel, arena, agentes contaminantes o restos de organismos microbiológicos (Nazaroff, 1993; Hun Yoon y Brimblecombe, 2001) pueden depositarse en el objeto durante su exposición, ya sean provenientes de los visitantes o del propio entorno del museo. Por otro lado, también puede aparecer en las superficies de los objetos partículas de materiales de embalaje y almacenamiento, o restos de tratamientos de restauración anteriores, así como puede ser necesaria la eliminación de una amplia variedad de productos de degradación, dependiendo del estado de conservación de dichos objetos.

El segundo paso en la selección de un método de limpieza específico para un objeto de plástico es la valoración del tipo de limpieza que se va a realizar. Dentro de los métodos de limpieza existen varias clasificaciones, referidas a las diferencias entre los aspectos prácticos de la limpieza. Por ejemplo, una clasificación extensamente aceptada es la distinción entre métodos de limpieza "mecánicos" y "químicos" (Wilks, 1987). Los métodos de limpieza mecánicos se refieren a "romper la adherencia de la suciedad y eliminarla" del objeto, e incluyen una larga lista de agentes abrasivos (tales como partículas de arena), limpieza física sin contacto con la superficie del objeto de arte (como aire comprimido), vibraciones (como ultrasonidos), paños, aspiradoras, etc. Por el contrario, los métodos de limpieza químicos implican reacciones químicas que rompen los enlaces dentro de las partículas, (enlaces entre las propias partículas de suciedad o enlaces entre las

partículas de suciedad y el sustrato), como las reacciones producidas por el agua, detergentes, solventes, limpiadores comerciales, geles, etc. Otro enfoque generalmente aceptado es la clasificación de los métodos de limpieza en "húmedos" y "secos" (Saulnier, 2002). Según este criterio, los métodos de limpieza en seco son aquellos que no implican líquidos, e incluyen el uso de partículas abrasivas, esponjas o paños. Por otro lado, los métodos de limpieza en húmedo se basan en el uso de líquidos, tales como agua, soluciones detergentes, disolventes orgánicos, productos de limpieza comerciales etc. Dentro de los métodos de limpieza en húmedo, existe una sub-clasificación referida al empleo de agua o disolventes orgánicos, definiéndose como agentes de limpieza "al agua" o "disoluciones orgánicas".

Otros tipos particulares de limpiezas fuera de las clasificaciones anteriores son: el uso de agentes biológicos llamados "enzimas" y la limpieza basada en el uso de láseres. Las enzimas son proteínas que catalizan reacciones naturales en los organismos vivos. Debido a la selectividad de las enzimas en esta acción catalítica, algunas se han utilizado para "romper" substancias orgánicas, con el fin de eliminarlas del objeto artístico. Las enzimas actúan sólo sobre un tipo particular de moléculas (llamadas "sustrato") sin afectar a otros materiales orgánicos de diferente naturaleza. Las enzimas usadas en restauración son enzimas proteolíticas, lipolíticas y glicosídicos que catalizan la hidrólisis de los enlaces químicos de proteínas, lípidos y polisacáridos, respectivamente. Debido a esta propiedad, estas enzimas pueden utilizarse como una alternativa a los ácidos y las bases que se emplean para la limpieza de sustancias poliméricas envejecidas en las obras de arte, tales como adhesivos naturales, películas de caseína, barnices etc. (Cremonesi, 1995). Por otro lado, los láseres se basan en la utilización para la ablación de la radiación láser pulsada, permitiendo el control preciso del nivel de limpieza de la superficie. Los láseres son dispositivos que emiten luz coherente, lo que permite centrarse en un punto de tamaño muy pequeño. La emisión de luz se basa en el proceso de emisión estimulada de radiación electromagnética y se caracteriza por alta intensidad, mono-cromaticidad (emisión en una longitud de onda muy estrecha) y la direccionalidad (Fotakis *et al.*, 2006).

Los parámetros más importantes a tener en cuenta cuando se utiliza un método de limpieza basado en la ablación por láser son: el coeficiente de absorción del material que va a ser eliminado, (el cual depende de la longitud de onda de la radiación láser emitida), y la magnitud de la energía del láser (expresada en J/cm^2). Estos dos factores determinan el nivel de limpieza de la superficie y la eficiencia de la limpieza (Koss y Marczak, 2005). Sin embargo, aunque esta técnica resulta útil en otras áreas del patrimonio cultural, no es muy adecuada para materiales plástico, ya que el margen de trabajo sin causar daño es bastante pequeño.

Debido a las propiedades químicas y físicas particulares de los materiales plásticos, y con el fin de evitar resultados adversos, hay varios factores que deben ser considerados inicialmente antes de seleccionar un método de limpieza. Estos factores son:

- Resistencia química del polímero;
- Temperatura durante la limpieza ;
- La tensión superficial del disolvente elegido para un sustrato determinado;
- El pH;
- Solubilidad de polímero en solución de limpieza;
- La volatilidad de los disolventes;
- El tiempo de limpieza.

La resistencia química de un polímero se refiere a la reacción química que experimenta un polímero específico cuando se somete a la acción de ciertos agentes químicos. Aunque la resistencia a la acción de agentes químicos, ambientes o radiación depende en gran medida de la naturaleza química y del tipo de enlaces químicos en el material, es aún más determinante la existencia de puntos débiles en la cadena polimérica, tales como defectos, ramificaciones o grupos terminales (Lampman, 2003). Por ejemplo, la ruptura hidrolítica es una vía de degradación importante en los polímeros semi-sintéticos, (como el nitrato de celulosa o de acetato de celulosa), por lo que deben evitarse las limpieza basadas en agua cuando

se limpien obras d arte compuesta de dichos materiales poliméricos (Keneghan y Egan, 2008). En resumen, la reactividad del plástico que va a ser limpiado debe ser considerada e investigada, con el fin de evitar daños durante el proceso de limpieza.

"Los materiales plásticos son sólidos rígidos y duros a temperaturas suficientemente bajas, sin embargo cuando sube la temperatura, los polímeros termoplástico adquiere suficiente energía térmica para permitir a sus cadenas moverse libremente y que se comporten como un líquido viscoso, siempre que no haya degradación" (Chanda y Roy, 2006). De este modo, cualquier proceso que implique cambios de temperatura en los polímeros debe ser controlado, ya que pueden afectar la estructura física del polímero. Los efectos en los polímeros debido a los cambios de temperatura dependen del rango de temperatura alcanzado, por lo que existen una serie de definiciones de tipos de temperatura asociadas a los diferentes cambios de fase en los polímeros. La temperatura de transición vítrea (Tg), es aquella a la que comienza a producirse la micro movilidad de los segmentos de cadena y las cadenas laterales, produciendo un reblandecimiento de los materiales termoplásticos, si bien son aun mecánicamente estable.

Por encima de la Tg, la movilidad molecular aumenta, lo que hace disminuir la resistencia mecánica del polímero (Klein, 2011). Esto significa que los polímeros se vuelven gomosos por encima de la Tg, mientras que se vuelven rígidos y quebradizos por debajo de la Tg. Por otra parte, los polímeros termoplásticos cristalinos se funden cuando se excede la temperatura de fusión cristalina (Tm), mientras que las resinas termoplásticas amorfas llegan a la fase de fundido por encima de la temperatura de flujo (Tf). Tras alcanzar el estado fundido, la degradación de ambos termoplásticos (amorfos y cristalinos), comienza por encima de la temperatura de descomposición Td (Klein, 2011). Por el contrario, los polímeros termoestables no tienen una Tm, lo que hace que no se reblandezcan, sino que se quemen cuando superan la Tg (Gómez Gonzáles, 1994).

Dado que algunos plásticos tienen su Tg próxima a la temperatura ambiente (Tabla 8; Odian, 2004), cualquier método de limpieza que implique acciones mecánicas (fricción) y aumento de la temperatura debe ser testado previamente con el fin de evitar la fusión del plástico, lo que causaría deformaciones y arañazos en las superficie debido al calor producido durante la limpieza (Chanda y Roy, 2006). Puesto que los arañazos son zonas vulnerables a la escisión de la cadena polimérica y de la mayor reactividad (debido al aumento del área de la superficie), son particularmente propensos a una reducción de la resistencia a la tracción y a un eventual fallo en la red polimérica, ocasionando una reducción en el brillo debido a la disminución de las propiedades de reflexión de luz (Keneghan y Egan, 2008).

Tabla 8.Temperaturas de transición vitrea (T_g) y de fusión cristalina de algunos polímeros.

Polymer	T_g (°C)	T_m (°C)
Polyethylene	-125	137
Polyoxymethylene	-83	181
Polyisoprene (natural rubber)	-73	28
Polyisobutylene	-73	44
Polypropene	-1	176
Poly(vinylidene chloride)	-18	200
Poly(vinyl fluoride)	41	200
Poly(hexamethylene adipamide) (nylon-6,6)	50	265
Poly(ethylene terephthalate)	61	270
Poly(vinyl chloride)	81	273
Polystyrene	100	250
Poly(methyl methacrylate)	105	220
Cellulose triacetate	105	306
Polytetrafluoroethylene (Teflon)	117	327

La energía de la superficie es otra propiedad importante a tener en cuenta durante la limpieza de un objeto de plástico, ya que se está relaciona con la humectabilidad de una superficie (de Gennes *et al.*, 2004), que se define como la tendencia de un líquido a extenderse sobre un sustrato sólido (Fujinami *et al.*, 2009). La humectabilidad depende de la relación entre la energía superficial del sustrato y la tensión superficial del disolvente. Para humedecer una superficie, la tensión superficial del disolvente debe ser inferior a la energía superficial del sustrato (Tabla 9).

Tabla 9.Energía libre superficial de los polímeros y tensión superficial de los disolventes.

Polymer	**Surface free energy at 20 °C [mN/m]**	**Solvent**	**Surface tension at 20 °C [mN/m]**
Polyamide-6,6 PA-66	46.5	Water	72.8
Polyvinylidene chloride PVDC	45	Glycerol (GLY)	64
Polyethyleneterephthalate PET	44.6	Formamide (FA)	58.2
Polyethyleneoxide PEO	42.9	Diethylene glycol (DEG)	44.8
Polyetheretherketone PEEK	42.1	Ethylene glycol (EG)	47.7
Polyvinylchloride PVC	**41.5**	Nitrobenzene	43.9
Polymethylmethacrylate PMMA	41.1	Carbon disulfid	32.3
Polyamide-12 PA-12	40.7	1-nitro propane	29.4
Polystyrene PS	40.7	Ethylbenzene	29.2
Polyvinylacetate PVA	36.5	Benzene	28.88
Polyethylene-linear PE	35.7	Chloroform	27.5
Polyethylene-branched PE	35.3	Tetrahydrofuran (THF)	26.4
Polycarbonate PC	34.2	Acetone (2-Propanone)	25.2
Polyisobutylene PIB	33.6	Methyl ethyl ketone (MEK)	24.6
Polypropylene-isotactic PP	30.1	Propanol 25 °C	23.7
Teflon™ PTFE	20	Methanol	22.7
Polydimethylsiloxane PDMS	19.8	Ethanol	22.1

Por ejemplo, en el caso del PVC, su energía superficial es inferior a la tensión superficial del agua (Tabla 9), y por tanto no se produce la humectación (Figura 12). Por el contrario, la tensión superficial del etanol es la mitad de la energía superficial de PVC (Tabla 9), lo que favorece que el etanol se extienda sobre la superficie de PVC (Figura 12). Muchos plásticos tienen una baja energía superficial, lo que conlleva una muy baja tensión de humectabilidad (Goss, 2010), dificultando que sus superficies puedan ser mojadas por un líquido. Por lo general, la energía de una superficie dada (medida en mN/m), se calcula mediante la medición del ángulo de contacto (θ) de la superficie con un líquido de tensión conocida. Este cálculo puede verse afectado por las tensiones interfaciales y por características del polímero tales como: la rugosidad de la superficie, la heterogeneidad química, el hinchado de la superficie, la disolución parcial del polímero, la orientación molecular, etc. (Augsburg, 1998).

El ángulo de contacto, que se define como el ángulo formado entre las interfaces líquido-vapor y líquido-sólido en la línea de contacto trifásica sólido-líquido-vapor, es una medida de la hidrofobicidad y humectabilidad de una superficie (Pesonen-Leinonen, 2005). Cuando el valor de ángulo de contacto es menor de 60º, la superficie tiende a estar completamente humectada. Po el contrario, una pobre humectabilidad de una superficie se produce cuando el ángulo de contacto es mayor de 90º.

La humectabilidad de una superficie también depende de la polaridad del disolvente o líquido utilizado para la limpieza. Los plásticos son principalmente hidrófobos, por lo que disolventes orgánicos no polares tienden a mojar mejor las superficies de los plásticos. Por el contrario, el agua y los disolventes polares tienden a formar gotas de esfera en la superficie, lo que dificulta el contacto entre el plástico y la solución de limpiadora.

Por ejemplo, un caso práctico del comportamiento de humectación de varios líquidos en una superficie de PVC plastificado comercial puede verse en la Figura 12, donde se observan los diferentes ángulos de contacto (θ), calculado mediante el método de la gota colgante, sobre la superficie de PVC. Así como el agua desionizada produce una mala humectabilidad del PVC plastificado (valores altos de θ) y tiende a formar gotas en la superficie del plástico, las soluciones acuosas básicas o detergentes disminuyen el valor de θ, aumentando la superficie de contacto entre el sólido y el líquido (Figura 12).

Por tanto, los agentes de limpieza recomendados para superficies plásticas deben tener una tensión superficial inferior a la del plástico, con el fin de lograr el contacto necesario entre ambas superficies y el proceso de limpieza tenga lugar. Otros factores que afectan la humectabilidad de una superficie y que deben ser considerados cuando se limpia una superficie plástica son: la tensión superficial, la viscosidad y la densidad del líquido, ya que son propiedades que afectan a su capacidad de difusión. Po otro lado, la rugosidad superficial y la cantidad de

impurezas también afectan a la capacidad de humectación, así como la temperatura puede modificar la viscosidad del líquido y por tanto afectar la facilidad con la que el líquido se propaga a lo largo de una superficie (Kumar y Prabhu, 2007). Todos estos factores externos e internos inherentes a las superficies deben tenerse en cuenta en cualquier proceso de limpieza.

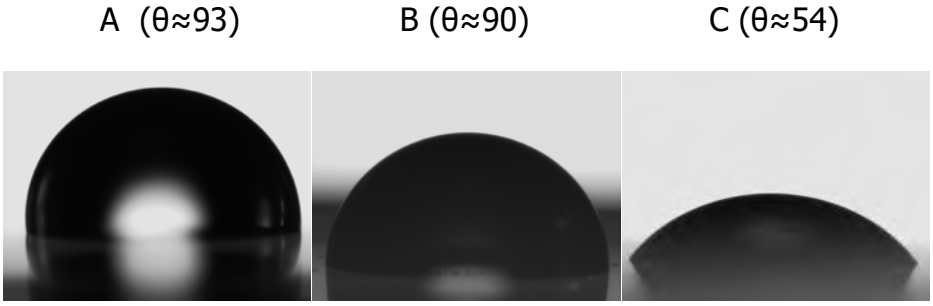


Figura 12. Medidas de Angulo de contacto de A) agua desionizada, B) KOH 1N y C) Dehypont LS45 5% en PVC plastificado.

Por otro lado, la degradación de los polímeros puede ser causada por reacciones químicas como la hidrólisis (Chanda y Roy, 2006), por lo que deben tenerse en cuanta cuando se decide un método de limpieza para una superficie plástica. Los polímeros que contienen grupos hidrolizables tales como ésteres, amidas y carbonatos son susceptibles al ataque del agua. Cuando estos grupos están presentes en la cadena principal, su hidrólisis se traducirá en una reducción del peso molecular el inicio del deterioro del polímero (Brydson, 1999). La velocidad de hidrólisis depende directamente de la pH (Leeuwen y van Vermeire, 2007), ya que los ácidos y bases catalizan las reacciones de hidrólisis. Por lo tanto, el pH de las soluciones de limpieza debe ser controlado con el fin de evitar daños en el objeto de plástico durante el proceso de limpieza.

La solubilidad se define como la cantidad máxima de soluto que puede ser disuelta en una cantidad dada de disolvente (Wilks, 1987). Para que una sustancia sea soluble en un disolvente, las fuerzas de atracción entre las moléculas de disolvente y la sustancia debe ser superior a las fuerzas de atracción entre las

moléculas dentro de la sustancia. Cuando se emplean disoluciones durante los procesos de limpieza, solo las partículas de suciedad deberían disolverse, mientras que el material que compone la obra de arte no debería verse afectado. Con el fin de evitar la disolución de los componentes de la obra de arte, el "Parámetro de solubilidad de Hildebrand" (δ), puede utilizarse para predecir la solubilidad de una sustancia en un disolvente particular (Tabla 9). Dicho parámetro de solubilidad viene expresado como $MPA^{1/2}$ (en unidades del SI) y se define como la raíz cuadrada de la densidad de energía de cohesión, que es un reflejo directo del número de fuerzas de van der Waals que mantienen unidas las moléculas del líquido (Burke, 1984) δ se expresarse como:

$$\delta = [(\Delta H_v - RT)/V_m]^{1/2}$$

Donde ΔHv es la entalpía de vaporización, Vm es el volumen molar, RT es la constante universal de los gases y T es la temperatura absoluta (este término es obtenido de la entalpía de vaporización necesaria para lograr la energía de vaporización, Balmares et al., 2004).

El parámetro Hildebrand ha sido calculado para muchos disolventes (Tabla 10; Burke, 1984) y sustancias, incluyendo materiales plásticos (Tabla 11; Rudin y Choi, 2012), y se basa en el siguiente principio: "dos compuestos son solubles sólo cuando su parámetros de solubilidad están muy cerca el uno al otro". En otras palabras, cuanto mayor distancia exista en los valores de los parámetros de Hildebrand del disolvente y del plástico, menor será el riesgo de la disolución de plástico. En el caso de objetos de plástico, debe tenerse en cuanta no sólo la solubilidad del material plástico en sí mismo, sino también la solubilidad de los aditivos que forman el total del material.

Tabla 10. Parámetros de solubilidad de Hildebrand para algunos disolventes.

Solvent	**δ, (MPa)$^{1/2}$**
n-Hexane	14.9
Toluene	18.3
Benzene	18.7
Acetone	19.7
Ethanol	26.2
Methanol	29.7
Water	48.0

Por lo tanto, los disolventes y disoluciones utilizados para la limpieza deben ser seleccionados de acuerdo a: 1) la solubilidad de las partículas que deben ser eliminadas del objeto artístico, 2) la solubilidad del plástico en necesidad de limpieza y 3) la solubilidad de los aditivos que se encuentran presentes en el plástico. Esto significa que los disolventes y disoluciones seleccionados para la limpieza deben sólo disolver la suciedad o partículas a eliminar, sin disolver ni el polímero ni cualesquier otra sustancia que forme parte del mismo, tales como aditivos, plastificantes etc. Un ejemplo según los valores que se muestran en las Tablas 10 (Burke, 1984) y 11 (Rudin y Choi, 2012), sería el poli (cloruro de vinilo) y la acetona. Puesto que el parámetro de solubilidad de ambos es muy próximo, no es recomendable el uso de acetona para la limpieza de PVC, ya que lo disolvería, causando daños irreversibles.

Una extensión del parámetro del Hildebrand es el parámetro Hansen (Tabla 12; Hansen, 1967; Burke, 1984), que considera no sólo las fuerzas de dispersión (δ_d^2), sino también los enlaces de hidrógeno (δ_h^2) y los componentes polares (δ_p^2) (Leeuwen, 2007; Belmares *et al.*, 2004). Por tanto, el parámetro de Cohesión Total de Hansen sería la suma de estos tres componentes:

$$\delta_t^2 = \delta_d^2 + \delta_h^2 + \delta_p^2$$

Tabla 11. Parámetros de solubilidad de Hildebrand para algunos polímeros.

Polymer	δ, $(MPa)^{1/2}$	H-Bonding Group[a]
Polytetrafluoroethylene	12.7	Poor
Polyethylene	16.4	Poor
Polypropylene	17	Poor
Polyisobutylene	17	Poor
Polybutadiene	17.2	Poor
Polystyrene	18.4	Poor
Poly(methyl methacrylate)	19.0	Medium
Poly(vinyl acetate)	19.7	Medium
Poly(vinyl chloride)	19.9	Medium
Cellulose diacetate	23.3	Strong
Poly(vinyl alcohol)	26.0	Strong
Polyacrylonitrile	26.0	Poor
Nylon-6,6	28.0	Strong

a Composition of copolymers are in parts by weight

Los parámetros de solubilidad de Hansen son determinados empíricamente basándose en múltiples observaciones experimentales de la solubilidad. Sin embargo, para polímeros, los parámetros de Hansen son asignados a los parámetros de aquel disolvente que causa la máxima hinchazón del polímero según en una serie de experimentos de absorción de disolventes por el polímero. Por tanto, se espera que los parámetros de Hildebrand y de Hansen para un polímero sean similares pero no idénticos y aunque ambos son utilizados para expresar la solubilidad, sus valores pueden no ser idénticos, ya que han sido calculados mediante diferentes métodos (Chanda y Roy, 2006).

Tabla 12. Parámetros de solubilidad de Hansen y radios de interacción para algunos polímeros y resinas.

Polymer (trade name, supplier)	δd $(MPa)^{1/2}$	δp $(MPa)^{1/2}$	δh $(MPa)^{1/2}$	R $(MPa)^{1/2}$
Cellulose acetate(Cellidore® A, Bayer)	18.6	12.7	11.0	7.6
Chlorinated polypropylene(Parlon® P-10,Hercules)	20.3	6.3	5.4	10.6
Epoxy (Epikote® 1001,Shell)	20.4	12.0	11.5	12.7
Isoprene elastomer (Ceriflex®IR305, Shell)	16.6	1.4	-0.8	9.6
Cellulose nitrate1/2 sec,H-23, Hagedorn)	15.4	14.7	8.8	11.5
Polyamide, thermoplastic (Versamid® 930, General Mills)	17.4	-1.9	14.9	9.6
Poly(isobutylene)Lutonal® IC-123, BASF)	14.5	2.5	4.7	12.7
Poly(ethylmethacrylate)(Lucite® 2042, DuPont)	17.6	9.7	4.0	10.6
Poly(methyl methacrylate)(Rohm and Haas)	18.6	10.5	7.5	8.6
Polystyrene (Polystyrene LG, BASF)	21.3	5.8	4.3	12.7
Poly(vinyl acetate)(Mowilith® 50, Hoechst)	20.9	11.3	9.6	13.7
Poly(vinyl butyral)(Butvar®B-76, Shawnigan)	18.6	4.4	13.0	10.6
Poly(vinyl chloride)(Vilpa® KR, k=50, Montecatini)	18.2	7.5	8.3	3.5
Saturated polyester(Desmophen® 850, Bayer)	21.5	14.9	12.3	16.8

Cuando los tres parámetros de Hansen son tratados como coordenadas para definir un punto en tres dimensiones, se obtiene el centro de una esfera de solubilidad (δ_d, δ_p, δ_h) y su correspondiente radio interacción (R). Los líquidos cuyos parámetros se encuentran dentro del volumen de esta esfera son disolventes activos para dicho polímero. Un polímero es probablemente soluble en un disolvente (o mezcla de disolventes) si los parámetros de Hansen para el disolvente se encuentran dentro de la esfera de solubilidad del polímero (Burke, 1984). Los disolventes con solubilidades de Hansen similares son miscibles en casi todas las proporciones; valores distintos dan lugar a solubilidades limitadas. Por tanto, los parámetros de solubilidad de Hildebrand y Hansen son útiles para la selección de disolventes y aditivos en las formulaciones, para la mezcla de polímeros, para el control de la cinética y para la distribución de la secuencia del monómero en copolímeros (Balmares *et al.*, 2004).

Otro factor clave en cualquier proceso de limpieza es la volatilidad del disolvente, que depende su viscosidad y tensión superficial. Los líquidos que tienen una baja viscosidad y una baja tensión superficial tienden a tener una alta volatilidad, por lo que la duración del contacto entre el líquido y la superficie en necesidad de limpieza es corto. Por otro lado, los líquidos con una viscosidad y tensión superficial altas, tienen una volatilidad baja, lo que les permite interactuar con la superficie durante un período de tiempo más largo (Wilks, 1987). Con el fin de evaluar la rapidez de evaporación de los disolventes, deben tenerse en cuenta: la presión de vapor, el punto de ebullición y el calor latente. De este modo, cuanto mayor es la presión de vapor y menor el punto de ebullición y el calor latente, más volátil es un disolvente (Gómez Gonzáles, 1994). En algunos casos, es necesario el empleo de limpiezas prolongadas para poder eliminar la suciedad de la superficie, para lo cual pueden emplearse los denominados *"solvent-based-gels"* (Stulik *et al.*, 2004; Gels Cleaning Research, 1998-2003) desarrollados por Richard Wolbers, que disminuyen la volatilidad del disolvente y ofrecen beneficios importantes tales como: ser una alternativa a ciertos disolventes tradicionales o métodos mecánicos, y un mayor control y selección de la limpieza respecto a otros métodos.

Durante la limpieza de materiales plásticos, el tiempo de limpieza (la duración del contacto entre el líquido y el plástico) debe ser supervisado debido al impacto directo, tanto positive como negativo, que tiene sobre el material. A pesar de que los tiempos limpiezas prolongados pueden ser mas más eficientes en la eliminación de suciedad respecto a los tiempos de limpiezas breves, pueden producir consecuencias adversas para la superficie del plástico. Por ejemplo, los objetos pueden absorber las disoluciones limpiadoras si éstas permanecen durante un tiempo prolongado en contacto con la superficie del objeto, o si el objeto que se encuentra inmerso en la disolución limpiadora. Este es el caso del PVC, el cual es insoluble y químicamente estable en agua, pero puede absorberla e hincharse cuando se sumerge en agua durante un período prolongado de tiempo (Sale, 1988). Otro efecto adverso en los tratamientos de limpieza prolongados, es la extracción de aditivos mediante los disolventes o disoluciones detergentes. Del mismo modo, el riesgo de daño aumenta

con el aumento del tiempo de limpieza cuando se emplean métodos de limpieza en seco. Por ejemplo, cuando se emplean paños o cepillos suaves para la limpieza, las partículas eliminadas del objeto durante la acción de limpieza pueden quedar depositados en la tela o el cepillo, produciendo el rayado de la superficie si dichos objetos son utilizados sucesivamente en la limpieza. En estos casos, es importante seleccionar tiempos cortos de limpieza, así como el reemplazo continuado de los agentes de limpieza. Teniendo en cuenta todas estas consideraciones, resulta claro que el principal problema al limpiar objetos de plástico en los museos es determinar qué método de limpieza (mecánico, acuoso, químico, etc.) puede utilizarse de manera eficaz sin dañar el objeto. Dentro de la conservación de arte pueden encontrarse tratamientos generales y específicos en referencia a la limpieza de objetos plástico, de los cuales pueden extraerse las siguientes recomendaciones generales:

- Agua desionizada ha sido generalmente recomendadas para la limpieza de plástico (Fairbrass, 1999; Shashoua, 2008), aunque hay autores que recomiendan su uso con cautela, especialmente cuando se trata de la inmersión de los objetos de plásticos en agua (Sale, 1988), así como otros autores incluso desaconsejan el empleo de este disolvente para la limpieza plásticos y cauchos;

- Los disolventes orgánicos, (los cuales se utilizan normalmente para la limpieza de obras de arte en conservación), no se recomiendan para la limpieza de plásticos, debido a los riesgos de hinchazón, disolución y extracción de aditivos cuando se emplean en plásticos (Sale, 1988, Shashoua, 2008), aunque su uso específico en limpieza puntuales (tales como la eliminación de etiquetas antiguas o restos de adhesivos de trabajos de restauración anteriores), ha sido aceptado por varios investigadores (Quye y Williamson, 1999; Shashoua, 2008; Huys y van Oosten, 2005);

- Las disoluciones detergentes han sido sugeridas como agentes de limpieza para plásticos, aunque algunos autores han advertido sobre los efectos

negativos de su uso en ciertos tipos de plásticos. Por ello, es recomendable el empleo de disoluciones poco concentradas, así como su completa eliminación de la superficie de plástico una vez terminado el proceso de limpieza (Sale, 1988; Blank, 1990; Quye y Williamson, 1999);

- Limpieza en seco mediante hisopos de algodón, cepillos, trapos, aspiración, etc. ha sido generalmente aceptada como una práctica segura para la limpieza de obras de arte hechas de plástico (Williams et al, 1998; Shashoua, 2.008.). Por otra parte, algunos autores sugieren que la limpieza en seco es el "mejor método" de limpieza para plásticos y cauchos (Williams, 1997);

- No es recomendable ni la inmersión ni los enjuagues prolongados de los objetos de plástico durante los tratamientos de limpieza, así como se ha sugerido que las disoluciones limpiadoras sean aplicados con cuidado y eliminadas con rapidez (Quye y Williamson, 1999);

- Aunque con cierta controversia, los limpiadores comerciales han sido aceptados dentro de la comunidad de conservadores. En el caso de su empleo en materiales plásticos, algunos autores han recomendado su uso (Budden, 1991), mientras que otros han recomendado precaución cuando se utilizan en objetos plásticos en los museos (Shashoua, 2008), ya que la posibles consecuencias aún no han sido investigadas a fondo.

En el caso particular de obras de arte de PVC , varios autores han recomendado los métodos de limpieza en húmedo, aunque éstos son acompañados generalmente por acción mecánica, ya que los disolventes o soluciones de limpieza necesitan un medio portador (por ejemplo hisopos de algodón) para ser aplicados. En algunos casos, la limpieza en húmedo puede realizarse mediante el empleo de acciones no-mecánicas, como la inmersión de la obra de arte en una disolución limpiadora o disolvente, aunque esta práctica no es recomendable para PVC debido a los efectos negativos tales como la absorción de disolvente o la migración aditivos en las

disoluciones limpiadoras (Sale, 1988).

El método de limpieza en húmedo comúnmente aconsejado los para objetos de PVC es la limpieza mediante agua desionizada o desmineralizada (Fairbrass, 1999; Shashoua, 2008). A su vez, el empleo de surfactantes para la limpieza de PVC, tales como soluciones acuosas de detergentes no iónicos, también ha sido propuesto por algunos autores (Fairbrass, 1999; Huys y van Oosten, 2005), como es el caso de Synperionic N (C_9H_{19}-C_6H_4-$(CH_2CH_2O)_n$-OH) o Dehypon LS 45 (alcohol graso alcoxylado C_{12}-C_{14}, con aproximadamente 4 moles de óxido de etileno y aproximadamente 5 moles de óxido de propileno).

El empleo de disolventes orgánicos no ha sido aconsejado para la limpieza de PVC debido a la interacción con el propio polímero o sus aditivos (Sale, 1.988). La acetona, por ejemplo, es capaz de disolver el PVC, por lo que debe ser evitada en la limpieza de PVC (Shashoua, 2008). Sin embargo, algunos disolventes orgánicos, como xileno o ShellSol A100 (Huys y van Oosten, 2005) han sido propuesto para la eliminación de adhesivos degradados o restos de restauraciones anteriores de la superficie de obras de arte de PVC. Basándose en el empleo de métodos acuosos utilizados tradicionalmente para la limpieza de superficies pictóricas (Wolbers, 2000), el uso de micro-emulsiones de agua con un agente tensioactivo y un disolvente orgánico con un parámetro de solubilidad diferente a la de PVC, han sido investigadas recientemente como métodos de limpieza de PVC plastificado (Hackett, 2014). Este hecho abre nuevas posibilidades en el uso de mezclas para la limpieza de obras de arte de PVC, como por ejemplo la mezcla de ECOSURF 3, el tensioactivo HLB (Hydrophilic–Lipophilic Balance), decametilciclopentasilo (disolvente no polar) y agua desionizada.

11.4. Técnicas analíticas para el análisis de polímeros.

Como se explica en los capítulos anteriores, para la correcta conservación de una obra de arte se necesita información detallada de su composición. Además, cualquier objeto artístico que va a emprender un tratamiento de restauración debe ser cuidadosamente examinado y analizado antes de la aplicación del tratamiento. Sólo de esta manera, es posible evitar los daños irreversibles o la modificación del material de la obra de arte. Al analizar una obra de arte, se debe evitar en la medida de lo posible la sustracción de cualquier pieza del objeto artístico para el análisis, y sólo llevarlo a cabo cuando sea absolutamente necesario. En estos casos, el muestreo debe realizar principalmente en las partes ocultas de la obra y mediante la captación de piezas que ya se desprenden de la original.

Con base en el impacto que el muestreo tiene sobre las obras de arte originales, las técnicas analíticas se pueden dividir en dos categorías principales: las técnicas destructivas y no destructivas. Las técnicas no destructivas son aquellas que permiten la información analítica que se obtiene sin ningún daño a la muestra (Janssens y Van Grieken, 2004). En otras palabras, cuando se utiliza una técnica no destructiva la muestra puede ser utilizada de nuevo para el análisis, ya que no se produce la destrucción o modificación de la muestra. Ejemplos de análisis no destructivo son la Reflexión total atenuada (ATR), espectroscopía de rayos X de difracción (RXD) o rayos X Fluorescencia (XRF). Además, las técnicas no destructivas se pueden clasificar entre no invasivas, cuando no se requiere tratamiento adicional del objeto a medir e invasivas cuando sí se requiere. La microscopía electrónica de barrido (SEM), por ejemplo, es una técnica invasiva porque necesita tanto el muestreo del objeto como el posterior tratamiento de la muestra, en este caso el bombardeo iónico (al menos para las muestras no metálicas tales como los polímeros), a pesar de que la muestra se puede volver a analizar si es necesario. Por otro lado, la espectroscopia infrarroja con transformada de Fourier (FTIR) es una técnica no invasiva, ya que se puede aplicar directamente sobre la superficie de obras de arte, sin necesidad de muestreo.

Por otro lado, las técnicas destructivas son aquellas que implican el muestreo de una parte del objeto y la muestra se destruye durante la medición., debido a la necesidad de una preparación de la muestra (por ejemplo, la digestión). Estos métodos son, por ejemplo, las técnicas cromatográficas (cromatografía de gases, GC, cromatografía líquida, LC, cromatografía de permeación en gel, GPC), calorimetría diferencial de barrido (DSC), análisis termogravimétrico (TGA), etc. Dentro de las técnicas analíticas destructivas también existen las "técnicas de micro-analíticas", que examinan una parte microscópica del objeto siendo necesario solo la destrucción de una pequeña parte del objeto sin causar ningún daño visual (Van Grieken y Janssen, 2005). En microanálisis las cantidades analizadas son de aproximadamente 5 mg y 0,1 ml (Stuart, 2007). Estas técnicas son muy útiles cuando es estrictamente necesario el tomar muestras del objeto a analizar, pero la cantidad que se puede muestrear es muy limitada. Otros ejemplos son la espectroscopia láser de ruptura inducida (LIBS) o la ablación láser con detección de espectroscopía de masas con plasma acoplado por inducción (LA-ICP-MS).

Idealmente, se prefiere el uso de técnicas que se pueden aplicar directamente en la obra, sin necesidad de muestreo (Cucci *et al.*, 2011). Por otro lado, para que un procedimiento analítico pueda ser considerado no invasivo, se requiere no sólo que no se tomen muestras del objeto analizado, sino también que el objeto no se mueva de su ubicación normal, lo que presenta un riesgo de daño accidental (Sarrazin *et al.*, 2009). Además, los lugares donde la medición debe llevarse a cabo pueden ser no fácilmente accesibles, y el costo de instalación y mantenimiento de múltiples instrumentos pueden ser altos (Down y Lehr, 2004). Con el desarrollo actual de la ciencia y la tecnología informática, es posible hacer uso de equipos portátiles, cuyo tamaño y peso permitirá medir in situ, sin necesidad de muestreo o mover el objeto a un laboratorio.

Para ello, se ha desarrollado en los últimos años una gama de equipos móviles (Anglos y Karidas, 2009; Picollo *et al.*, 2014) y son cada vez más comunes en los laboratorios de conservación y museos (Shashoua, 2001; Chércoles Asensio *et al.*

2009; Miliani *et al.*, 2006). Estos equipos móviles pueden incluir varias técnicas analíticas como la radiografía de rayos X (XRF), imágenes multiespectrales, RMN portátil, FTIR o espectroscopía Raman.

Algunas de las ventajas de los equipos portátiles sobre los instrumentos convencionales son por ejemplo: son más pequeños y ligeros, y por tanto pueden ser fácilmente transportados a cualquier lugar, pueden trabajar con baterías y/o la red eléctrica, se evita la necesidad de muestreo, son más simples de utilizar y ocupan menos espacio en el laboratorio. Por otro lado, el equipo portátil es en general menos sensibles que los convencionales (McMahon, 2007) y también puede ser más caros. Por lo tanto, cuando se considera el uso de unos instrumentos portátiles o convencionales, se deben tener en cuenta varios factores, tales como: costos, requisitos físicos y la participación logística (Down y Lehr, 2004).

Sin embargo, las técnicas no destructivas solas pueden no siempre proporcionar una caracterización suficientemente detallada de las muestras (Prati *et al.*, 2010). Dado que los plásticos son materiales muy complejos que pueden incluir tanto materiales orgánicos e inorgánicos en su composición, deben de ser utilizadas diferentes técnicas analíticas instrumentales para la identificación de ambos, los polímeros y los aditivos que componen los materiales plásticos (Stuart, 2007).

Como se detalla en la Tabla 14, se puede lograr información muy diversa relacionada con materiales plásticos a través de ambas técnicas no destructivas y destructivas. Para la identificación de los polímeros, plastificantes, compuestos de degradación orgánicos y poliméricos y aditivos orgánicos, se pueden usar técnicas tales como FTIR, Raman o GC acoplado a espectroscopía de masas. Por otra parte, los compuestos inorgánicos dentro de los plásticos (rellenos, pigmentos, estabilizadores organometálicos etc.) pueden ser identificados por medio de difracción de rayos X, XRF o SEM, junto con espectroscopia de rayos X de energía dispersiva (EDX). Por lo tanto, para una caracterización completa del polímero, es

necesario el uso de más de una técnica de análisis y por tanto, entender la base de cada técnica analítica y la información que cada uno pueda proporcionada.

Tabla 14: Métodos analíticos para la caracterización de los plásticos.

	DSC	FTIR	FTIR RAMAN	(py) GC-MS	GPC	IC	SEM-EDX	TGA	XRD	XRF
Organic compounds	✓	✓	✓	✓	✓	✓	✗	✓	✗	✗
Inorganic compounds	✗	•	✓	✗	✗	✓	✓	✗	✓	✓
Polymer identification	✗	✓	✓	✓	✗	✗	✗	✗	✗	✗
Laminate identification	•	•	•	✓	✗	✗	✗	✗	✗	✗
Plasticizer identification	✗	✓	✓	✓	✗	✗	✗	✗	✗	✗
Inorganic filler identification	✗	•	✓	✗	✗	✗	✓	✗	✓	✓
Organic filler identification	✗	•	•	✓	✗	✗	✗	✗	✗	✗
Other organic additives	✗	•	•	✓	✗	✓	✗	✗	✗	✗
Other inorganic additives	✗	•	•	✗	✗	✓	✓	✗	✓	✓
Organic degradation products	✗	✓	✓	✓	✗	✓	✗	✗	✗	✗
Inorganic degradation products	✗	•	✓	✗	✗	✓	✓	✗	✓	✓
Gaseous degradation products	✗	✗	✗	✓	✗	✗	✗	✓	✗	✗
Polymer degradation	✓	✓	✓	✓	✓	✗	✗	•	✗	✗
Plasticizer loss	✗	✓	•	✓	✗	✗	✗	✓	✗	✗
Filler degradation	✗	✗	✗	✗	✗	✓	✓	✗	•	✓

Legend: Suitable ✓ Possible • Unsuitable ✗

En la espectroscopía infrarroja por transformada de Fourier (FTIR) se obtiene un espectro mediante la irradiación de una muestra con energía de la región infrarroja (λ = 1 mm a 750 nm) y midiendo qué fracción de la radiación incidente es absorbida en una energía particular. La radiación IR es absorbida más eficientemente cuando su frecuencia coincide casi exactamente con la frecuencia de movimientos internos dentro de una molécula. Para la radiación con frecuencias en el IR, los

movimientos relevantes de la molécula son las vibraciones de enlaces atómicos (Varella, 2013). En el caso de materiales plásticos, se pueden identificar por FTIR tanto el polímero como los plastificantes, así como la degradación del polímero y los aditivos orgánicos. Además del análisis cualitativo, por medio de esta técnica se pueden lograr mediciones cuantitativas que se puede utilizar para la cuantificación de la pérdida de plastificante (Derrick *et al.*, 1999).

Mientras que la espectroscopia IR depende de un cambio en el momento dipolar permanente del enlace químico o de la molécula con el modo normal de vibración con el fin de producir la absorción, la espectroscopía Raman depende de un cambio en el momento dipolar inducido o la polarización para producir la dispersión Raman. Cuanto más simétrica es la molécula, mayores son las diferencias entre el IR y espectros Raman (Koenig, 1999). Mediante ambas técnicas, se puede obtener información complementaria y valiosa no sólo acerca de la composición de polímero, sino también en su conformación. La región espectral IR del espectro electromagnético incluye radiación con números de onda que van desde alrededor de 14.000 a 20 cm^{-1}, pudiéndose dividir en las subregiones del cercano (NIR), medio (IR o infrarrojo medio) y lejano (FIR) (Derrick *et al.*, 1999). Una técnica superficie de IR común para polímeros es la espectroscopia de reflectancia total atenuada (ATR), también llamada espectroscopia de reflexión interna (IRS) o reflectancia interna múltiple (MIR) (Scheirs, 2000).

Los requisitos de muestra para espectroscopia ATR es que la muestra sea lisa, plana y flexible con el fin de tener un contacto adecuado entre el ATR y la muestra y evitar la reducción de la intensidad de las bandas de absorción a altas frecuencias debido a un contacto no óptimo. Por lo tanto, la espectroscopia ATR es particularmente útil para polímeros que son suaves y pueden ser presionados fácilmente contra el cristal reflexión interna (Scheirs, 2000). Debido al hecho de que la espectroscopia ATR es una técnica analítica superficie, es ideal para la detección de la contaminación y la degradación de una superficie de polímero (Scheirs, 2000).
La cromatografía es la separación de mezclas moleculares por distribución entre dos

o más fases: una fase estacionaria (una superficie) y una fase móvil que pasa a través de que la columna que contiene la fase estacionaria. En la cromatografía de gases (GC) la fase estacionaria puede ser líquida o bien (cromatografía gas-líquido) (cromatografía gas-sólido) sólido (Cheremisinoff, 1996) y el gas portador es por lo general un gas inerte (nitrógeno o helio). La muestra se inyecta generalmente a alta temperatura para asegurar la volatilización y se analiza en este estado, lo que podría ser una limitación. La mezcla de analito se separa en función de la afinidad de los diferentes componentes con la fase estacionaria. Por lo tanto, cuanto mayor sea la interacción con la fase estacionaria, mayor será el tiempo que se tarda en eluir, en salir de la columna, también llamado "tiempo de retención". La cromatografía líquida (LC) utiliza bombas de alta presión para pasar un disolvente líquido presurizado que contiene la mezcla de muestra a través de una columna rellena con un material adsorbente sólido (Snyder *et al.*, 2.009).

En la actualidad, la espectroscopia de masas (MS) acoplada a ambas técnicas de separación, GC y LC, es uno de los sistemas de detección que permiten analizar los componentes separados de la mezcla, mediante la medición de la relación de masa a carga y la abundancia de los iones en fase gaseosa. Cuando se analizan los plásticos, el acoplamiento con MS se puede utilizar para la identificación de mezclas de polímeros, plastificantes, productos de degradación y aditivos orgánicos (Quye y Williamson, 1999; Hanton, 2001).

La permeación en gel (GPC), la cromatografía de exclusión por tamaño también llamado (SEC) y la cromatografía de iones (IC) son las configuraciones de LC que más se utilizan en la caracterización de polímeros. Por medio de la GPC, las moléculas en solución pasan a través de columnas de relleno con partículas muy pequeñas, redondas y porosas y se separan en su camino a través. Por lo tanto, la GPC se utiliza para determinar la distribución del peso molecular promedio de una muestra de polímero, así como puede ayudar a obtener información cualitativa sobre ramificaciones de cadena larga o determinar la distribución de la composición de copolímeros (Cheremisinoff, 1996). IC es un método cromatográfico de separación

de iones, realizado en una columna rellena con un material de intercambio iónico sólido para separar los iones orgánicos e inorgánicos, así como aniones y cationes (Fritz y Gjerde, 2009) orgánicos más grandes. IC se basa en la interacción entre las moléculas que eluyen a través de la columna y el soporte sólido en la columna. Cuanto más fuerte es la interacción iónica (basado en la diferencia de cargas entre la columna y las moléculas de la muestra) más alta es la retención en la columna cromatográfica.

Los efectos de difracción se observan cuando la radiación electromagnética incide sobre estructuras periódicas con variaciones geométricas en la longitud de la escala de la longitud de onda de la radiación (Birkholz, 2005). Por lo tanto, cuando la radiación electromagnética o corpuscular es difractada por la materia, se produce un patrón de difracción o diagrama de dispersión (Günzler y William, 2001). La difracción de rayos X (XRD) generalmente se ocupa de la materia cristalina (ya sea monocristales o polvos cristalinos), y así se pueden detectar con esta técnica los compuestos inorgánicos depositados en la superficie de plástico, tales como rellenos, sales, productos de degradación cristalinos, etc. (Quye y Williamson, 1999). En el caso de cristales de polímeros, los patrones de difracción son debidos al hecho de que las moléculas, en este caso las cadenas de polímero, en lugar de átomos, se ajustan los puntos de la red de las células unitarias (Mitchell, 2004). En los polímeros semicristalinos, que generalmente se describen como que consta de una fase cristalina y una fase amorfa, la fase cristalina se puede determinar mediante XRD (Chung y Smith, 2000). El índice cristalino (CI) es una medida relativa de la cristalinidad: CI = Aa * 100 / (Ac + Aa) donde Ac es el área de los picos cristalinos, Aa el área bajo los picos amorfos y (Ac + Aa) es la intensidad total dispersada (Smith, 1999).

Las técnicas de dispersión de energía de rayos X (EDX) y de fluorescencia de rayos X (XRF) se utilizan para la identificación de cargas inorgánicas, pigmentos y productos de degradación inorgánicos en materiales plásticos (Quye y Williamson, 1999). Ambas técnicas, EDX y XRF, se basan en los mismos principios: la muestra es

incidida con una irradiación (un haz de electrones en EDX y un haz de rayos X de alta energía en XRF), crea un puesto vacante de electrones, que se vuelve a llenar por un electrón de los orbitales más altos de energía, liberando energía (Dieing *et al.*, 2011). Y se liberan rayos X secundarios con una energía específica y constante que es única para cada elemento.

Otras técnicas utilizadas para caracterizar materiales plásticos son la Calorimetría Diferencial de Barrido (DSC) y el análisis gravimétrico térmico (TGA). La DSC es una técnica donde se mide la diferencia en la entrada de energía a una muestra y un material de referencia mientras que la muestra y la referencia se someten a un programa de temperatura controlada (Cheremisinoff, 1996). Se registran tanto el flujo de la temperatura como el calor asociado con las transiciones de la muestra en función del tiempo y la temperatura. Estas mediciones proporcionan información cualitativa y cuantitativa sobre los cambios físicos y químicos que involucran procesos endotérmicos o exotérmicos, o cambios en la capacidad de calor como la transición vítrea, la fusión y la cristalización (Varella, 2013). En los polímeros, el principal uso de los análisis de DSC es la detección y cuantificación del proceso de fusión cristalino y el cálculo del grado de cristalinidad de un polímero (Sepe, 1997). Por otro lado, el análisis TGA mide la cantidad y la velocidad de los cambios de peso en un material como una función de la temperatura o el tiempo (Sepe, 1997). Por medio de esta técnica, se puede cuantificar la pérdida de plastificante, la pérdida de relleno, % peso de carga, etc.

La espectroscopía de resonancia magnética nuclear (RMN), es una técnica que se utiliza para la determinación de la estructura de muestras desconocidas sobre la base de las propiedades magnéticas de los núcleos atómicos (Günther, 2013). El desplazamiento químico del núcleo se define como la relación entre la frecuencia de absorción para dicho núcleo de interés, y la frecuencia de absorción de una molecular normal (Ghosal y Srivastava, 2009). Dado que el entorno químico afecta a las propiedades magnéticas de los núcleos atómicos medidos, si existen átomos idénticos o grupos funcionales adyacentes darán diferentes señales de RMN

("desplazamiento químico"), proporcionando información sobre la estructura de la molécula. Los espectros de RMN de ^{13}C e ^{1}H son los más utilizados en química y bioquímica, a pesar de que, los núcleos ^{19}F, ^{14}N y ^{31}P también proporcionan información valiosa (Günther, 2013). En el caso de los polímeros, la RMN proporciona análisis cualitativos y cuantitativos, aunque la aplicación esta espectroscopía de RMN se extiende incluso más allá de la caracterización química, llegando a la investigación de los fenómenos físicos como la cinética, la dinámica y la morfología (Brandolini y Hills, 2000).

11.4.1. Análisis y caracterización del PVC.

Al igual que cualquier otro plástico, la identificación de PVC debe llevarse a cabo siguiendo un enfoque sistemático: pruebas preliminares, detección de elementos, la determinación de los valores característicos y, por último, las técnicas analíticas específicas. Para una identificación exacta, sin embargo, la muestra de ensayo debe primero ser purificada para eliminar aditivos (plastificantes, cargas, pigmentos, etc.) que puedan afectar a los resultados de un análisis (Chanda y Roy, 2006). En el caso de polímeros de PVC, la purificación se puede conseguir mediante extracción del plastificante y aditivos de la mezcla de polímeros, por ejemplo por medio de éter di-isopropílico (Shashoua, 2001).

Una prueba específica para polímeros que contienen cloro, como el PVC, es la prueba de Beilstein, que consiste en la identificación del color de una pequeña pieza de material de prueba en un alambre de cobre calentado sobre un quemador Bunsen (Williams, 2000). La presencia de halógenos (cloro, bromo, yodo) se detecta por el color verde producido como consecuencia de la volatilización del haluro de cobre. En el PVC no plastificado el olor del ácido clorhídrico será notable, mientras que el olor del plastificante será evidente cuando se quema PVC plastificado (Patrick, 2005). Otra prueba para la identificación de poli (cloruro de vinilo) es el punto de ebullición de sus soluciones de piridina con unas gotas de hidróxido de sodio metanólico (5%).

En una prueba positiva, se forma con el tiempo, una coloración marrón y precipitados de color marrón oscuro (Chanda y Roy, 2006). La densidad puede también utilizarse en las pruebas de flotación de agua para determinar si se hunde, sin embargo otros polímeros como acrilonitrilo-butadieno-estireno y policarbonato tienen densidades similares (Patrick, 2005).

Para obtener resultados más precisos y sensibles se debe utilizar técnicas de análisis cromatográficas tales como GC o LC. Sin embargo, la aplicación de la cromatografía de gases para polímeros está restringida debido a su alta masa molecular y baja volatilidad (Haken, 1998) y se hace necesario una etapa previa de pirólisis de la muestra. La pirólisis consiste en calentar la muestra hasta que se degrada y libera fragmentos moleculares de baja masa (Seidel, 2008), que luego se pueden separar cromatográficamente y se identifican mediante espectrometría de masas. Por medio de la altamente sensible GC-MS es posible separar e identificar el plastificante dentro del polímero PVC, así como la presencia y la cantidad de especies de bajo peso molecular en un compuesto de resina o de vinilo (Shashoua, 2001; Seidel, 2008).

La técnica de NMR se ha utilizado ampliamente para el análisis de polímeros, proporcionando información sobre la estructura molecular, dinámica de la cadena, la cristalinidad, la formación de la red y la cadena de entrelazamiento (Seidel, 2008). En el caso particular de PVC, los estudios con esta técnica han demostrado la presencia de importantes regiones ordenadas dentro de la cadena de PVC, y en última instancia, la formación de las regiones microcristalinas (Wilkes et al., 2005).

La identificación del tipo de grupo funcional presente en un polímero se logra por métodos espectroscópicos como el FTIR, la ATR y la espectroscopia Raman. En el PVC en particular, se ha estudiado con frecuencia con la espectroscopia de FTIR porque su espectro de IR contiene información exhaustiva sobre el contenido configuracional y conformacional de la muestra (Koenig, 1999). Por lo tanto, la espectroscopia de FTIR se ha empleado ampliamente para determinar las principales

características químicas de la molécula de PVC, incluyendo determinaciones de tacticidad del polímero (Wilkes *et al.*, 2005), mientras que la ATR-FTIR permite explorar la superficie del PVC (Seidel, 2008). No sólo se pueden identificar las bandas infrarrojas correspondientes al PVC, sino también las que vienen del aditivo unido al polímero de PVC. La tabla 15 recoge las principales bandas de infrarrojos típicas de un polímero de PVC en ausencia de aditivos y algunos aditivos comunes (Wilkes *et al.*, 2005; Tabb y Koenig, 1975).

Tabla 15: Bandas de infrarrojo de PVC.

Peak Assignment	**Wavenumber (cm^{-1})**
Aliphatic CH_2 and C-H stretching (PVC)	2971, 2911
CH_2 bending (wag) (PVC)	1435 (amorphous), 1427 (crystalline)
C-H in CHCl (PVC)	1330
C-H in CHCl (PVC)	1254
C-C stretching (PVC)	1098
CH_2 rocking (PVC)	967
C-Cl stretching (PVC)	693
C-Cl stretching (PVC)	616 (amorphous), 636 (crystalline)
TiO_2	500-1000 (Broadening)
$CaCO_3$	876
Acrylic impact or flow modifier	1733-1734
styrene/acrylonitrile (SAN) flow modifier	2238
Plasticizer (C=O)	1726
Plasticizer (CH stretching)	3000

Como se mencionó antes, la espectroscopía IR depende de un cambio en el momento dipolar permanente del enlace químico o molécula, mientras que el Raman depende de un cambio en el momento dipolar inducido o polarización y con la combinación de ambas técnicas es posible obtener información completa sobre la conformación de los polímeros. En el caso particular del polímero de PVC, se puede distinguir la estructura amorfa y cristalina por medio de estas técnicas (Wypych,

2008), así como se han detectado dos estructuras conformacionales sindiotácticos (extendida y plegada) (Koenig, 1999).

Además, la espectroscopía Raman de resonancia es una técnica espectroscópica adicional que se utiliza para la investigación de estructuras moleculares. Se produce el espectro de intensidad mejorada cuando la frecuencia de excitación láser se aproxima a la de una transición electrónica permitida en la molécula que está siendo examinado. Esos modos normales que son vibracionalmente activos exhiben una mejora muy pronunciada de sus intensidades en un factor tan grande como 10^4 o 10^5 (Bowe y Maddams, 1989) y generalmente se asocian con el cromóforo electrónico que está excitado (Koenig, 1999). En el caso de PVC, la espectroscopía Raman de resonancia se utiliza para evidenciar signos de degradación debido a la formación de secuencias de polienos conjugados que actúan como cromóforos.

Para la investigación química del polímero PVC y sus aditivos, se pueden usar varias técnicas. Se ha utilizado la espectroscopía de Infrarrojo Cercano (NIR) para analizar la composición de compuestos de vinilo y determinar la identidad y el nivel de mezclas de plastificantes en las formulaciones. También se han utilizado métodos térmicos basados en las mediciones de las propiedades del polímero como una función de la temperatura o el tiempo a temperatura constante (Seidel, 2008), como por ejemplo el DSC, para caracterizar la transición vítrea de compuestos de vinilo y para determinar el nivel de estabilidad (Wilkes *et al.*, 2005).

11.4.2. Estudio de la superficie del PVC

La correcta selección de técnicas apropiadas es un aspecto importante durante el examen de una superficie de plástico, no sólo en función del tipo de material bajo investigación, sino también en el tipo de información que deben alcanzarse. Un resumen de algunas técnicas comunes que se utilizan para la caracterización superficial de PVC y la información proporcionada por cada técnica se muestra en la

Tabla 16 (Stamm, 2008).

Tabla 16: Técnicas más empleadas para la caracterización de la superficie.

Technique	**Probe In / out**	**Smallest information depth / width (nm)**	**Information**	**Comments**
X-Ray photoelectron spectroscopy XPS	X-Rays / electrons	5 / 3000	Chemical composition, binding state	Quantitative, vacuum technique, lateral imaging possible
Scanning force microscopy (SFM) or Atomic force microscopy (AFM)	Cantilever	0.05 / 1	Surface topography, composition, toughness	Atomic resolution, many different modes
Electron microscopy	Electrons	2/1	Surface topography	Vacuum technique
Optical microscopy OM	Light	0.1/300	Surface roughness, structure	Many possibilities, good height resolution with interference techniques

En la espectroscopia de rayos X de fotoelectrones (XPS), una técnica analítica de superficie basada en el efecto fotoeléctrico, la superficie de la muestra se bombardea con fotones de baja energía mono-energética (fotones de rayos X) (Bart, 2006) que resulta en la emisión de un nivel básico de electrones (fotoelectrones). La energía de enlace del electrón es el parámetro que identifica cada electrón específicamente, tanto en términos de su elemento padre y nivel de energía atómica. El espectro de fotoelectrones de rayos X inducido es la gráfica de la intensidad de fotoelectrones en función de la energía de electrones. (Watts y Wolstenholme, 2003). Dado que ninguno de los elementos comparten el mismo conjunto de energías de enlace, los equipos de medición de las energías cinéticas de fotoelectrones ofrece análisis elemental (Günzle y William, 2001). La mayoría de los

sistemas poliméricos se pueden examinar con éxito en un XPS convencional. Sin embargo, algunas desventajas de las técnicas de XPS son, por ejemplo, el uso de equipo costoso, algunos daño por radiación a los materiales sensibles de rayos X o pobre resolución de profundidad (Bart, 2006).

La microscopía óptica (OM) o microscopía de luz utiliza la luz visible y un sistema de lentes para ampliar las imágenes de pequeñas muestras. Un microscopio de luz ordinaria no está bien adaptado para el estudio de la estructura 3D de una muestra. Presenta una imagen 2D que consiste en una superposición de regiones de enfoque y de desenfoque de la muestra. Para solucionar esto se ha desarrollado la microscopía confocal, evitando que la luz desenfocada llegue al detector (Bart, 2006). La microscopía de luz puede funcionar en el modo de transmisión, donde la radiación pasa a través de la muestra y se recoge en el otro lado, lo que requiere una muestra fina o en el modo de reflexión en donde la luz se recoge de la superficie, permitiendo que las muestras sean más gruesas (Sawyer *et al.*, 2008). La microscopía de luz transmitida revela la estructura interna de un material transparente y puede ser utilizada en el examen de fibras individuales, la morfología y orientación de las partículas. También se puede utilizar en el examen de secciones finas de revestimiento resinoso. La microscopía de luz reflejada se utiliza para examinar la morfología de la superficie. Las superficies rugosas y aquellas en las que el brillo o la transparencia no es de importancia u opacos pueden ser examinados con éxito utilizando métodos de luz reflejados simples (Bart, 2006).

Dentro de la microscopía electrónica, hay dos técnicas principales: la microscopía electrónica de barrido (SEM) y microscopía electrónica de transmisión (TEM). En general, la SEM proporciona imágenes de la morfología externa de apariencia similar a las formadas por el ojo humano, mientras que la TEM sondea la estructura interna de sólidos y da acceso a los detalles microestructurales o ultra-estructurales no familiares para el ojo humano (Goodhew *et al.*, 2000). Por medio de tanto la SEM y la microscopía TEM se puede obtener no sólo información estructural sino también química.

Mientras la OM produce imágenes ampliadas a través de las lentes de cristal y luz visible o ultravioleta, los "microscopios electrónicos" producen imágenes ampliadas por el uso de lentes electrostáticas o electromagnéticas con electrones en rápido movimiento como fuente de iluminación, proporcionando alta o muy alta resolución (Watt, 1997). La primera clase de la microscopía electrónica se basa en un haz incidente estacionaria a lo largo de una dirección fija, como la microscopía electrónica de transmisión convencional (CTEM), mientras que el segundo tipo se basa de una sonda de electrones bien dirigida a través de la muestra, tales como la microscopía electrónica de transmisión de barrido (STEM), microscopía electrónica de barrido (SEM) o espectroscopia de electrones Auger (AES)/microscopía Auger (SAM). Los métodos de haz estacionario se basan en procesos de formación de la imagen, mientras que los métodos de exploración son esencialmente técnicas de "mapeo" (Günzler y Williams, 2001).

La formación de imágenes en el SEM depende de la adquisición de señales producidas por la interacción del haz de electrones y la muestra (Zhou y Wang, 2007). Dentro de la espectroscopía SEM, hay dos tipos de métodos para producir imágenes: por los electrones secundarios (producida cuando el haz primario golpea la superficie de las muestras y los electrones se emiten desde los átomos excitados por el haz) y por electrones retrodispersados, que son electrones incidentes que se dispersan elásticamente por el átomo de muestra a un ángulo de más de 90º (Zhou y Wang, 2007).

Al comparar la microscopía electrónica con microscopía de luz, las microscopías SEM y TEM tienen mayores capacidades de resolución, así como una gama de la ampliación más ancho y más alto que la OM (Tabla 17, Flegler *et al.*, 1993). Sin embargo, los microscopios electrónicos requieren funcionamiento a condiciones de muy alto vacío, con la excepción de microscopía electrónica de barrido ambiental (ESEM), y las muestras examinadas a menudo requieren una preparación más extensa que la necesaria para la OM.

Tabla 17: Propiedades principales de la microscopía SEM, TEM y la óptica.

Feature	OP	TEM	SEM
General Use	Surface morphology and sections (1-40 μm)	Sections (40-150 nm) or small particles on thin membranes	Surface morphology
Source Illumination	Visible Light	High-speed electrons	High-speed electrons
Best Resolution	ca. 200 nm	ca. 0.2 nm	ca. 3-6 nm
Magnification Range	10-1,000x	500-500,000x	20-15,000x
Depth of field	0.002-0.05 nm (N.A. 1.5)	0.004-0.006 mm (N.A. 10^{-3})	0.0031 mm
Lens Type	Glass	Electromagnetic	Electromagnetic
Image ray-formation spot	On eye by lenses	On phosphorescent plate by lenses	On cathode tube by scanning device

Por otro lado, la técnica de microscopía de fuerza atómica (AFM) puede resolver los átomos individuales y puede operar a presión atmosférica o incluso bajo el agua, y no requiere preparación de la muestra más allá de la creación o la exposición de una superficie de interés (Sawyer et al., 2008). En la AFM, la sonda consiste en una punta aguda que se localiza al final de un brazo flexible denominado *cantilever* (Seidel, 2008). La AFM funciona poniendo en contacto la punta "en voladizo" con la superficie. Las fuerzas de repulsión iónica de la superficie doblan la punta "voladiza" hacia arriba. Y así se obtiene una imagen topográfica de la muestra mediante el trazado de la deflexión del voladizo en comparación con su posición en la muestra (Butt *et al.*, 2005). Otra característica de los microscopios AFM es que no tienen lentes y construyen las imágenes punto por punto (Sawyer *et al.*, 2008).

Cuando las técnicas de OM, SEM, TEM y AFM se utilizan para la caracterización de superficie del polímero se obtienen muy diferentes rangos de resolución como se puede observar en la Tabla 18 (Sawyer *et al.*, 2008). Además, debe considerarse que, contrariamente a la microscopía óptica y las microscopías de sonda de barrido (por ejemplo la AFM), la microscopía electrónica de radiación a menudo cambia el polímero durante la formación de imágenes, que puede afectar a la interpretación de la imagen. Sin embargo, cada técnica tiene sus propios beneficios que deben ser

comprendidos en profundidad (Sawyer et al., 2008).

Table 18: Rangos de estudio para la microscopía SEM, AFM y la óptica

Technique	Size ranges
Optical Microscopy (OM)	200nm – 200µm
Scanning Electron Microscopy (SEM)	4nm - 4mm
Transmission Electron Microscopy (TEM)	0, 2nm – 0, 2mm
Atomic Force Microcopy (AFM)	0, 2nm – 0, 2mm

A diferencia de la microscopía óptica, la profilometría confocal tiene la capacidad de crear una imagen nítida de la región de enfoque de la muestra, proporcionando imágenes 3D de superficies rugosas y desiguales. La profilometría es esencialmente un microscopio confocal que obtiene un alto número de imágenes a diferentes alturas focales en la topografía de la superficie y crea una imagen 3D (Hamilton y Wilson, 1982; Lange *et al.*, 1993). "Ópticamente" secciona la superficie y mediante tratamientos informáticos se transforma estas secciones en imágenes digitales y finalmente un mapa topográfico (Lange *et al.*, 1993). El microscopio confocal funciona haciendo coincidir geométricamente dos puntos focales conjugados en el espacio de la imagen. Cuando los dos puntos, un punto de origen y un punto final, se corresponden, satisfaciendo la condición confocal, el punto de origen se fotografiará con máxima intensidad. Si los puntos no se corresponden y son desplazados de los lugares de enfocado, el detector de punto rechaza la luz dispersada ampliada y detecta una intensidad menor (Cha *et al.*, 2000). Se pueden crear 'costuras' adicionales de varias exploraciones a partir de superficies contiguas a partir de las imágenes profilométricas, lo que permite el examen de áreas mucho más amplias que con SEM o AFM. Se podría decir que la profilometría confocal complementa imágenes SEM y supera la profundidad de las limitaciones del campo de la microscopía óptica (van den Berg *et al.*, 2008). En la Tabla 19 (Malacara, 2007), se recoge un resumen de las diferencias entre la microscopía de barrido en túnel (STM), el interferómetro óptico de luz blanca y la microscopía confocal

(Malacara, 2007).

Tabla 19: Principales características de la microscopía de barrido en túnel (STM), el interferómetro óptico de luz blanca y la microscopía confocal.

	AFM/STM	**White light interferometric**	**Confocal microscopy**
X, Y resolution	2-10 nm AFM 0.1 nm STM	0.5 μm (NA objective dependent)	0.5 μm (NA objective and lateral sampling dependent)
Z resolution	0.1 nm AFM 0.01 nm STM	0.3 nm	1-20 nm (Dependent on objective magnification)
Field of view	70-150 μm	100 x 100 μm to 10 x 10 mm but can be extended by stitching	100 x 100 μm to 10 x 10 mm but can be extended by increasing lateral sampling lens array objective
Measurable height range	Up to 20 μm	8 mm (or limited by working distance of objective)	Limited by working distance of objective
Sample preparation	Minimal	None	None
Contact with the sample	Optional	No	No
Special surface requirements	STM-only conductive surfaces	Needs correction for dissimilar materials and film coatings	Needs correction for dissimilar materials and film coatings
Scanning	Point by point	Full field of view	Point by point
Full field dynamic motion of sample measurement	No	Yes	No

Through the glass measurement	Not possible	Possible	Possible
Film thickness	Only if film has a step	Minimum 0.1 μm	Minimum 1 μm
Measurable optical properties of surface film	Indirectly through correlation with topography	Yes	Yes
Other measurable material	Numerous: adhesive, electric, magnetic, visco-elastic, elastic etc.	No	No

Entre las técnicas utilizadas para el examen superficial descritas anteriormente, la SEM, la OM y la AFM han sido las más ampliamente aplicadas a la caracterización del PVC (Kuisma, 2006). La SEM, por ejemplo, ha puesto de manifiesto características importantes en la morfología de partículas de polímeros de suspensión, de masa y de dispersión de PVC, mientras que la OM se ha utilizado para determinar la porosidad relativa de partículas de PVC en suspensión, haciendo uso de software de análisis (Wilkes *et al.*, 2005).

Por otra parte, la AFM ha sido utilizada en numerosos estudios como una técnica para la caracterización de la superficie de PVC (Kuisma et al., 2005), proporcionando imágenes de alta resolución y la información pertinente relativa a la adsorción, la adhesión y otros fenómenos que dominan en la superficie (Seidel, 2008). Se puede obtener más información sobre topografía de la superficie por medio de profilometría (Wilson, 1995), que proporciona no sólo imágenes 2D y 3D, sino también parámetros de rugosidad utilizados para la completa caracterización de la topografía de la superficie (Figura 13).

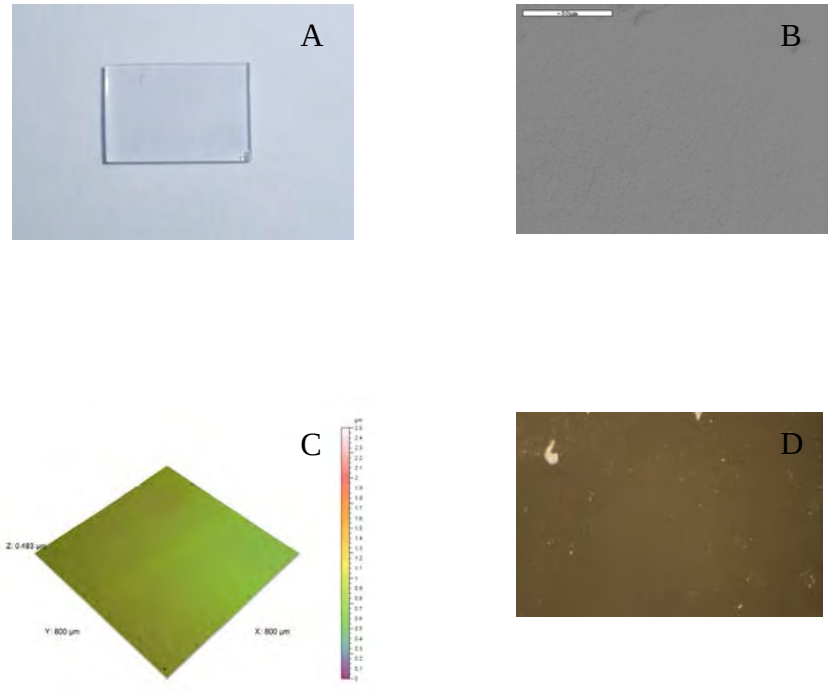


Figura 13: PVC plastificado (A) a simple vista, (B) caracterizada por SEM, (C) por profilometría y (D) con microscopía óptica.

11.4.3. Técnicas analíticas para el estudio y cuantificación de la limpieza.

En la industria, la verificación de la limpieza se lleva a cabo por medio de métodos instrumentales que van desde técnicas de bajo costo, tales como mediciones de ángulo de contacto o recuentos de partículas (Määttä et al. 2007), a técnicas más caras, que proporcionan la cuantificación limpieza y la composición química del contaminante, tales como FTIR, SEM/EDX o espectroscopía de rayos X fotoelectrónica (XPS) (Kuisma *et al.*, 2005, Kanegsberg y Kanegsberg, 2000). En el caso de una obra de arte, la limpieza debe ser libre de riesgo y garantizar que no hay daños a la superficie. De este modo, la superficie tiene que ser examinada después

de la limpieza con el fin de verificar no sólo la limpieza, sino también la idoneidad del método de limpieza en términos de conservación de la obra de arte.

Para el examen de las superficies de obras de arte después de los tratamientos de limpieza, se han utilizado técnicas, tales como la observación a simple vista o técnicas de examen de superficie comunes, tales como, OM, SEM-EDX, AFM, o profilometría confocal para el examen físico y visual de la superficie (Fairbrass, 1999; Huys y van Oosten, 2005; Gaspar *et al*., 2003; van den Berg *et al.,* 2008; Ioanid *et al*., 2011). Entre ellos, el ojo humano proporciona información directa sobre la superficie (Stout y Blunt, 2000) y todavía es un método común de evaluación (Gaspar et al., 2003). Sin embargo, el nivel de detalle proporcionado a menudo no es suficiente para una evaluación fiable de los efectos de limpieza. Por lo tanto, para obtener información más precisa acerca de la limpieza, se pueden obtener imágenes en 2D y/o en 3D por medio de otras técnicas como se ha descrito anteriormente. Además, los cambios en el brillo y color se utilizan a menudo para determinar el impacto de los tratamientos de limpieza en las superficies limpiadas.

En el caso de obras de arte de plástico, los dos principales métodos de examen para la evaluación de los efectos de limpieza y la investigación de los cambios producidos en las superficies de plástico es la OM (Huys y van Oosten, 2005; Fairbrass, 1999) y la medición del brillo (Shashoua, 2011). En general, el brillo puede ser definido como la capacidad de una superficie para reflejar la luz especular. Los materiales con superficies lisas, tales como plásticos, parecen altamente reflectantes (brillantes), mientras que las superficies muy rugosas no reflejan ninguna luz especular y, por tanto, aparecen mate. Al limpiar los plásticos, se pueden producir daños tales como arañazos, fusión de la superficie o la perdida de aditivos, lo que lleva a cambios de apariencia de la superficie en términos de brillo. Al tomar una medición inicial, cada valor registrado después se puede comparar con el valor numérico inicial para evaluar la cantidad de brillo que se ha perdido. La pérdida de brillo puede ser crucial para la apariencia de la obra o presentación, además de para la preservación. Para la determinación del brillo, se utiliza un medidor de brillo de

acuerdo con la norma ASTM D523. La luz se refleja desde la superficie hacia un detector en un ángulo de 20°, 60° o 85°, dependiendo de la reflectancia de la superficie (Lampman, 2003).

Aspectos más relacionados a la conservación de obras de arte y los museos, como las limitaciones de muestreo o la movilidad de la técnica instrumental, juegan también un papel importante durante el examen de limpieza. Como se ha descrito anteriormente, las técnicas que requieren toma de muestras del material, tales como SEM o ATM, harán más restrictivos en su uso que los que se puede aplicar directamente en la obra sin la resta de material, tal como la microscopía óptica, o profilometría.

Además, se han utilizado otras técnicas analíticas para la investigación química de la superficie de obras de arte después de los tratamientos de limpieza, como por ejemplo FTIR (Ioanid *et al.*, 2011), o la investigación de la eliminación de la suciedad y la presencia de residuos por medio de técnicas como espectroscopía de rayos X (EDX) (Gaspar *et al.*, 2003). Aparte del examen de las consecuencias de la limpieza, cualquier proceso de limpieza implica necesariamente la cuantificación de la limpieza en términos de eficiencia. La limpieza se puede determinar mediante el análisis de una muestra representativa con técnicas analíticas elegidas, a partir de datos recogidos durante un período de tiempo y en comparación con el rendimiento de las diferentes muestras (Kanegsberg y Kanegsberg, 2000). La comparación entre tratamientos de limpieza se debe basar en los parámetros clave asociados con la limpieza de superficies (Gaspar et al., 2003). En la conservación, a pesar de que generalmente se sigue utilizando la simple vista para evaluar la eficacia de la limpieza por medio de los parámetros habituales de percepción visual humana, los parámetros a ser medidos para determinar y cuantificar el nivel de limpieza son el color, el brillo y el ángulo de contacto (Shashoua et al., 2011, Levédrine *et al.*, 2012).

El espacio de color CIELAB (CIE 1976 L* a* b*) se propuso para cuantificar la

distribuciones de potencia espectral, que se perciben como color uniforme mediante las coordenadas CIELAB (L* a* b*). L* representa un componente de la luminosidad muy próximo a la percepción humana, mientras que a* y b* son las dimensiones de colores opuestos (CIE 15: 2004). La magnitud y el signo de las llamadas "diferencias de color" ΔL*, Δa*, Δb* se expresan como (Kang, 2006):

ΔL^* { > 0 = Claro; < 0 = Oscuro

Δa^* { > 0 = Rojizo; < 0 = Verdoso

Δb^* { > 0 = Amarillento; < 0 = Azulado

Las coordenadas CIELAB se calculan a partir de los valores triestímulo; por tanto, las condiciones del iluminante-observador deben se especificadas durante la medición (Berger-Schun, 1994). La diferencia de color se calcula mediante una fórmula estandarizada que permite indicar cuantitativamente el valor aproximado de la diferencia de color percibida entre dos colores dados (Klein, 2010):

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Asimismo, índices calculados a partir de las medias de los valores de L* de una muestra, también han sido utilizados para la cuantificación de la limpieza en aplicaciones de pavimentos industriales (Redsven et al., 2003), lo que puede ser utilizado como una herramienta para comparar los resultados obtenidos a partir de diferentes métodos de limpieza:

$$\text{Cleaning Index } (\%) = \frac{(L^*_{cleaned} - L^*_{soiled})}{(L^*_{unsoiled} - L^*_{soiled})} \times 100$$

Según se expresa mediante esta fórmula, cuanto mayor es el valor del Índice de Limpieza, más eficiente es el método de limpieza utilizado.

Como se ha mencionado anteriormente, el ángulo de contacto también ha sido utilizado en conservación para la cuantificación de la limpieza de las superficies de plástico. El ángulo de contacto θ puede ser definido en función de la humectabilidad del sólido por ese líquido, de este modo, ángulos cercanos a cero significan que el líquido se ha extendido y humedecido completamente la superficie (Brass, 1999), mientras que ángulos de contacto mayores de 90° indican una pobre humectabilidad de la superficie de plástico por el líquido, el cual no se extiende por la superficie, lo que probable mente no resulte en la adhesión del líquido a la superficie (Shashoua , 2008). La medición del ángulo de contacto como método para la cuantificación de la limpieza, se basa en los cambios de las energías superficiales inducidos por la limpieza, tales como los residuos de los agentes de limpieza, daños superficiales como arañazos, etc. (Shashoua *et al.,* 2011).

12. OBJETIVOS

12.1. Objetivos de la investigación.

Continuando la introducción anterior, el objetivo del presente trabajo ha sido la investigación sobre la limpieza de superficies nuevas y degradadas de PVC plastificado, con la intención de encontrar una metodología de estudio reproducible y aplicable a la limpieza de objetos realizados en plástico.

Los principales objetivos propuestos fueron:

1) Desarrollo de una metodología de estudio aplicable a la limpieza de obras de arte,
2) Determinación de métodos de limpieza efectivos y seguros para PVC plastificado, tanto en estado degradados y no degradado,
3) Determinación de nuevos métodos de cuantificación de la efectividad de los métodos de limpieza en materiales plásticos, así como su testeo en PVC plastificado,
4) Aplicación de los métodos de limpieza y de cuantificación obtenidos durante la investigación en objetos reales de PVC,

Objetivos secundarios del presente trabajo fueron:

1) Evaluación de los métodos de limpieza en PVC plastificado comercial, en vez de en muestras fabricadas en laboratorio,
2) Testeo en PVC plastificado de limpiadores en seco comercializados para la limpieza de plásticos,
3) Investigación del mecanismo de degradación del PVC plastificado comercial utilizado como modelo en el presente trabajo,

12.2. Organización y alcance de la tesis.

La estructura de la tesis fue diseñada siguiendo los objetivos descritos en la sección 2.1. Para ello, el primer paso fue la selección de un plástico común en las obras de arte que se encuentran en museos y colecciones de arte. Dado que PVC plastificado es un plástico común en museos, fue propuesto como material a utilizar como modelo en el presente trabajo. Contrariamente a la utilización de muestras fabricadas en el laboratorio, un PVC comercial fue utilizado en los experimentos, de modo que se evitasen situaciones irreales donde la composición de los objetos realizados en plástico es normalmente desconocida o parcialmente identificada en museos y colecciones de arte. Para ello, PVC flexible e incoloro manufacturado por al compañía Danesa VINK fue utilizado en la parte experimental.

Basándonos en el término "limpieza", tanto muestras sin signos de suciedad como muestras en diferentes estados de suciedad fueron incluidas en la investigación. Para ello, el PVC comercial fue sometido a un proceso de ensuciamiento natural y utilizado como material muestra en los test de limpieza. Asimismo, la degradación del material también debe tenerse en cuenta durante la limpieza de plásticos, siendo la temperatura y el foto-envejecimiento los factores mas señalados en la degradación del PVC. Durante la presente investigación, la foto-degradación fue considerada como causa principal de degradación, ya que la temperatura normalmente es monitorizada y controlada en los museos y colecciones de arte. Para ello, muestras del PVC comercial fueron sometidas a un proceso de envejecimiento artificial y utilizadas en los test de limpieza.

El siguiente paso en la metodología fue la selección de técnicas de limpieza para las muestras de PVC plastificado, mediante una profunda revisión de la bibliografía especifica sobre la limpieza de PVC plastificado y la investigación sobre los agentes de limpieza adecuados para el PVC plastificado. Los agentes de limpieza seleccionados incluyeron disoluciones orgánicas y acuosas en diferentes

concentraciones, detergentes, soluciones limpiadoras comerciales y agentes de limpieza en seco.

El objeto de esta selección no fue solo el análisis de los métodos de limpieza utilizados habitualmente en las obras de arte realizadas en plástico, sino también la investigación de nuevos métodos de limpieza específicos para PVC plastificado.

Asimismo, diferentes técnicas de análisis y de examen fueron seleccionadas para la investigación de los resultados después de la realización de las diferentes limpiezas. Siguiendo los criterios en conservación de arte, todas las técnicas seleccionadas fueron no destructivas, así como fueron aplicadas a temperatura ambiente y bajo condiciones de presión normales en laboratorio, garantizando la seguridad de uso para los objetos de arte.

Puesto que la limpieza es una acción que ocurre generalmente en superficie, sólo fueron seleccionadas técnicas que proporcionan información de la capa superficiales de las muestras. Para ello, la espectroscopía ATR-FTIR, de tan solo unas micras penetración en la superficie y de posible aplicación directa sobre el objeto, fue utilizada para el análisis de las variaciones químicas producidas como consecuencia de la limpieza. Por otro lado, las modificaciones físicas y los cambios de color fueron identificados mediante técnicas no destructivas tradicionalmente utilizadas en conservación de arte (microscopia óptica y colorimetría), así como el examen de superficies irregulares u objetos tridimensionales fueron llevado a cabo mediante profilometría de no-contacto.

Conjuntamente a la evaluación física y química de los efectos producidos por la limpieza, el siguiente paso en la metodología fue la cuantificación de los resultados obtenidos de la aplicación de los diferentes métodos de limpieza, con el objetivo de evaluar la eficacia de los mismos. Para ello, se propuso el método utilizado tradicionalmente en conservación de arte basado en la medida del color de la superficie antes y después de la limpieza, llamado colorimetría.

Sin embargo, debido a las limitaciones que presentan las técnicas colorimétricas cuando no hay suficiente contraste entre la superficie y las partículas de suciedad, o cuando la superficie a examinar no es suficientemente plana, otros métodos alternativos fueron investigados. Para ello, la variación en la topografía fue propuesta como un factor medible y asociable a los efectos producidos por la limpieza, con objeto de encontrar un nuevo método adecuado para la cuantificación de los resultados de la limpieza en objetos de PVC.

Como ultimo paso en el presente trabajo, fue la aplicación de los resultados obtenidos de la investigación de la limpieza del PVC plastificado comercial en un objeto real de PVC. Para ello, una muñeca antigua compuesta de PVC plastificado y con signos evidentes de degradación fue limpiada siguiendo cada uno de los pasos descritos en la metodología inicialmente propuesta.

13. DISCUSION INTEGRADORA

13.1. Factores que afectan la limpieza de PVC.

Como se expone en las publicaciones recogidas en los capítulos 5 , 6 , 7 y 8, se comprobó que los resultados de la limpieza de PVC depende de los siguientes factores : a) la composición de los productos de limpieza y del PVC b) la topografía de la superficie, c) la naturaleza química tanto de la suciedad como de los productos de degradación .

13.1.1. Agentes de limpieza y composicion del PVC.

Modificación químico/física de la lámina de PVC comercial o residuos del agente de limpieza no se detectaron después del tratamiento de limpieza con agua, con la disolución acuosa de Hostapon T 5 %, con la disolución acuosa de KOH 1 % M o con el producto comercial Multiren. Sin embargo, residuos de la disolución 5 % en agua del detergente Dehypon LS45 quedaron en la superficie PVC plastificado debido a su menor solubilidad en agua (Capítulo 6). En el caso del producto comercial Brillianize - Kleenmaster, no se detectaron residuos cuando se utilizó en la lamina de PVC plastificado (Capítulo 6). Sin embargo, residuos de este limpiador comercial fueron visibles por medio de las imágenes en 3D obtenidos por profilometría cuando se probó en la muñeca de PVC plastificado (capítulo 7.1), debido probablemente a la diferente topografía de las superficies de PVC. A diferencia del PVC comercial, liso y plano, la superficie rugosa y desigual de la muñeca dificultó la eliminación del agente limpiador, que tendió a quedarse entre las irregularidades del perfil topográfico.

El espectro ATR-FTIR del PVC plastificado mostró cambios significativos después de la limpieza con disolventes orgánicos puros, tales como etanol, propanol o heptano, debido a la extracción de plastificante durante la limpieza (Capítulo 6 paper 6.1). Sin embargo , mezclas inocuas de disolventes orgánicos mezclados con agua en proporciones que no causaron ningún daño químico o alteración física del PVC plastificado se lograron por medio del " Índice de plastificante " definido en el

capítulo 6. Como resultado, la mezcla 2: 1 de agua-etanol resultó adecuado para la limpieza de PVC plastificado comercial.

Métodos de limpieza en seco produjeron la alteración física del PVC plastificado cuando el tejido del agente limpiador estaba compuesto por fibras de nylon 100% (capítulos 5 y 7.3). Estas alteraciones fueron visibles mediante microscopía óptica y profilometría. Los espectros ATR-FTIR del PVC plastificado también mostraron diferencias debido a la interacción física entre las fibras de poliamida y el plastificante . Además, las fibras de poliamida resultaron visibles en la superficie de PVC plastificado bajo microscopía óptica y mediante las imágenes profilométricas 3D, hecho que no ocurrió cuando los agentes de limpieza compuestos por fibras de algodón o poliamida-poliéster. Los agentes limpiadores en seco compuestos por fibras mezcladas de poliéster-nylon no mostraron alteraciones del PVC plastificado detectables mediante espectroscopia de ATR- FTIR, aunque si se detectó la alteración de la superficie mediante microscopía óptica y profilometría tras tiempos de limpieza prolongados. Bastoncillos de algodón causaron alteraciones físicas y químicas debido a la migración de plastificante a cualquier tiempo de limpieza (Capítulos 5 y 7.3), que fueron detectables mediante microscopía óptica, profilometría y espectroscopia ATR- FTIR.

Muestras comerciales de PVC sin plastificante en su composición mostraron una respuesta diferente a la limpieza en seco: arañazos en la superficie fueron visibles con todos los limpiadores en seco después de tiempos de limpieza largos, siendo más intensos cuando se utilizaron hisopos de algodón y agentes de limpieza compuestos por fibras de poliamida (Capítulo 7.3).

13.1.2. Topografía de la superficie.

Como se muestra en los capítulos 5, 7.1 y 7.3, la topografía de la superficie de PVC desempeñó un papel importante en la limpieza. Podría concluirse que los métodos de limpieza en seco sobre superficies lisas produjeron cambios significativos

en ambas muestras de PVC plastificado y no plastificados cuando la limpieza fue realizada durante tiempos prolongados (véanse los capítulos 5 y 7.3). Por otro lado, las superficies rugosas (tales como las de la muñeca de PVC investigada en los capítulos 7.1 y 7.2) fueron más propensas a retener los agentes de limpieza en las heterogeneidades de la superficie, siendo mas difícil controlar la acción de limpieza, en términos de homogeneidad, bajo estas circunstancias. Como se explicó en el apartado anterior, los residuos de limpiador comercial Brillianize-Kleenmaster fueron visibles a través de las imágenes en 3D obtenidos por profilometría, cuando se utilizaron en la muñeca de PVC plastificado (Capítulo 7.1), debido a su superficie irregular y rugosa.

13.1.3. Naturaleza química de la suciedad y los productos de degradación.

La suciedad proveniente del proceso de ensuciamiento natural, acumulada sobre el PVC plastificado (capítulos 5) e identificada como agentes contaminantes, partículas de polvo, fibras y arena, pudo ser eliminada parcialmente por los agentes de limpieza en seco utilizados en esta investigación. Sin embargo, diferencias en la homogeneidad de la limpieza fueron visibles por medio de las imágenes proporcionadas por la profilometría de no contacto. A través de estas imágenes se comprobó que los agentes limpiadores compuestos por fibras de poliéster-poliamida produjeron una limpieza más homogénea y eficiente en comparación a los agentes compuestos por fibras de poliamida o algodón. En el caso de la muñeca de PVC plastificado (capítulos 7.1 y 7.2), los métodos de limpieza en seco fueron completamente ineficaces, ya que la suciedad no se componía de partículas depositadas en la superficie, sino de material orgánico, tales como proteínas, ácidos grasos o polisacáridos, imbuidos en el PVC plastificado. En este caso, los métodos de limpieza en húmedo fueron eficaces, aunque no todos ellos en la misma medida. En cuanto a la eficiencia. Respecto a la eficiencia de los mismos, se detectaron grandes diferencias entre ellos debido a la naturaleza de la suciedad en la muñeca. Debido a

la naturaleza no polar de proteínas y ácidos grasos, el agua y las mezclas de alcohol-agua no resultaron muy eficientes.

Aunque los disolventes orgánicos pueden ser efectivos en la disolución de estos compuestos, no deben ser utilizados por el riesgo que suponen de extraer plastificantes. Sin embargo, las disoluciones acuosas de Hostapon T y KOH resultaron muy eficaces en la limpieza. En el caso de la Hostapon T, su naturaleza aniónica fue capaz de solvatar proteínas y lípidos, mientras que la disolución acuosa de KOH, debido a su fuerte carácter básico, produjo la hidrólisis de proteínas y ácidos moderados como lípidos. En el caso de los polisacáridos, éstos pudieron ser fácilmente disueltos mediante las disoluciones acuosas debido a su naturaleza hidrófila.

En términos de homogeneidad y fortaleza de la limpieza, las disoluciones de KOH produjeron una gra eliminación de suciedad, como lo demuestra la alta diferencia en la rugosidad (medida por el parámetro Sq) antes y después de la limpieza. Una acción de limpieza profunda también fue visible en las imágenes en 3D y el perfil de rugosidad proporcionados por profilometría (Capítulo 7.1). Por el contrario, la limpieza obtenida mediante la disolución acuosa de Hostapon T fue más homogénea y superficial.

La degradación de PVC comercial afectó tanto al polímero como los plastificantes. Derivados de la degradación del PVC se obtuvieron polienos, mientras que alcoholes de cadena larga , benzoatos y anhídrido ftálico se produjeron a partir del foto-envejecimiento de los di-alquil ésteres de ácido ftálico utilizados como plastificante (Capítulos 5 y 8). Para la eliminación de estos productos de degradación (Capítulo 5), los métodos de limpieza en seco resultaron insuficientes, mientras que los métodos de limpieza en húmedo fueron más efectivos y proporcionan una limpieza más homogénea. Sin embargo, al igual que en el caso de la muñeca, se obtuvieron diferentes resultados mediante los productos de limpieza debido a la naturaleza de los compuestos producidos por el envejecimiento del

material de PVC plastificado. Debido a la baja polaridad de los productos de degradación, la disolución detergente aniónica Hostapon T proporcionó una limpieza eficiente y homogénea, mientras que las disoluciones polares, tales como agua desionizada, etanol-agua 1:2 , Multiren o Brillianize-Kleenmaster resultaron ineficaces (Capítulo 6).

13.2. Investigación sobre la degradación.

13.2.1. Fotodegradación del PVC plastificado comercial.

De los resultados obtenidos mediante ATR- FTIR y GC- MS, los siguientes compuestos pudieron identificarse en el proceso de foto-envejecimiento del PVC plastificado comercial utilizado en la primera parte de la investigación:

- alcoholes, benzoatos y anhídrido ftálico producidos como consecuencia de la degradación del plastificante,
- alquenos producen de la degradación del polímero.

Asimismo, los resultados experimentales obtenidos durante el proceso de envejecimiento mostraron un aumento casi lineal de alcoholes C9, un aumento del anhídrido ftálico, no tan linear como en los alcoholes y una disminución de la concentración de los benzoatos. Un mecanismo Norrish II fue propuesto para explicar la formación de alcoholes a través de los benzoatos, que actuarían como intermedios.

Mediante espectroscopía ATR- FTIR, se observó la formación progresiva de compuestos en la superficie del polímero formados durante el proceso de envejecimiento artificial. Este hecho que fue apoyado por el aumento de la absorbancia a 400 a 500 cm^{-1} que pudo observarse en el espectro Vis-UV. Así mismo, estos hechos indicaron la creación de grupos cromóforos durante los procesos de

foto-envejecimiento, que condujo a una coloración amarillenta y pérdida de brillo de las muestras durante el proceso de envejecimiento.

En cuanto a la magnitud del proceso de degradación, todas las técnicas analíticas y de examen utilizadas en esta investigación concluyeron que los efectos del foto envejecimiento fueron menores durante las dos primeras semanas, mientras que un aumento significativo de la degradación se observó después de la segunda semana. Dado que el proceso de foto-envejecimiento reprodujo las condiciones de foto-degradación al aire libre, se pudo concluir que el material de PVC utilizado en esta investigación no debería ser expuesto durante más de dos semanas a entornos desprotegidos.

13.2.2. Degradación de la muñeca de PVC plastificado.

En contraste con el PVC plastificado comercial, la muñeca de PVC plastificado utilizada en la segunda parte de la investigación mostró no sólo suciedad visible de la superficie, sino también evidentes signos de degradación en forma de partículas blancas acumulados en varias áreas. Por medio de análisis ATR-FTIR y GC-MS, estas partículas se identificaron como una mezcla de ácidos palmítico ($C_{16:0}$) y esteárico ($C_{18:0}$), acompañados por los correspondientes ésteres de 2-etil-hexilo de ácido graso.

Basado en la composición de la muñeca y apoyado por la literatura, estos ácidos y ésteres acumulados en la superficie fueron identificados como lubricantes migrados desde el interior del polímero. Asimismo, el hecho de que sólo los ácidos grasos $C_{16:0}$ and $C_{18:0}$ fueron detectados en la superficie en comparación con los ácidos $C_{14:0}$ y $C_{12:0}$ pudo deberse a su mayor proporción en el lubricante. Por el contrario, no fue detectada la migración a la superficie del bis(2-etil-hexil-ftalato) ni des sus productos de degradación.

13.3. Conclusiones generales.

Como conclusión general puede afirmarse, que tras una investigación exhaustiva y mediante el desarrollo de una metodología de limpieza para obras de arte hechas de plástico, han sido posible la obtención de varios métodos de limpieza en seco y en húmedo específicos para obras de arte compuestas de PVC plastificado. Estos métodos de limpieza no sólo han demostrado ser seguros para el PVC plastificado, sino también efectivos en la eliminación de suciedad y productos de degradación. A su vez, mediante el presente trabajo ha sido obtenido un nuevo método no destructivo para la cuantificación de la eficacia de limpieza, así como se ha propuesto un enfoque novedoso para el diseño de soluciones de limpieza a la medida.

13.3.1. Metodología y conservación.

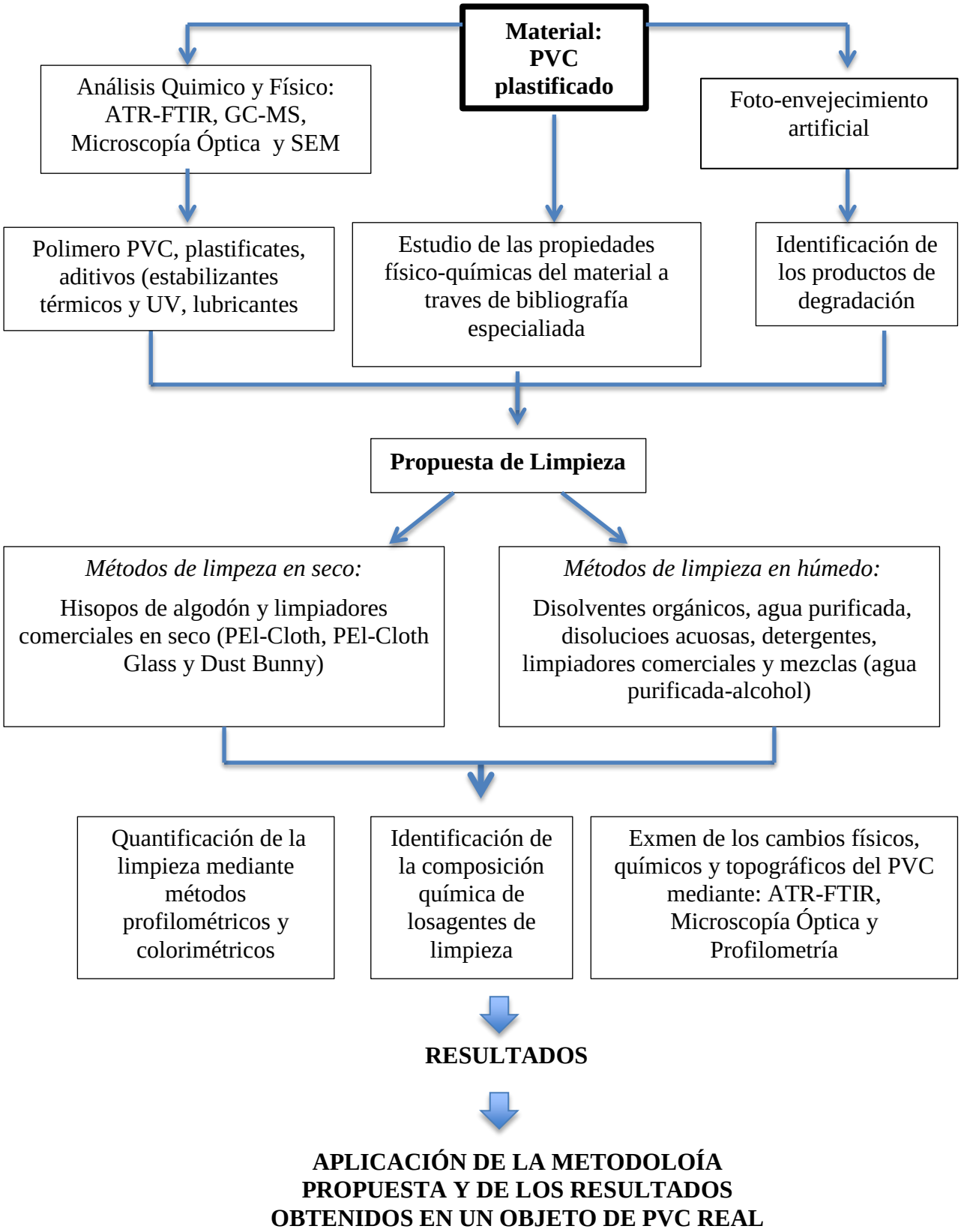
Una nueva metodología de estudio propuesta para la limpieza de objetos de plástico se ha aplicado con éxito en el presente trabajo, demostrando que pueden encontrarse productos de limpieza específicos para un material plástico en particular. Posteriormente, los pasos propuestos en la metodología fueron aplicados en el caso especifico de PVC plastificado, logrando productos de limpieza adecuados y eficientes para este material.

A diferencia de otros trabajos de investigación, se han utilizado para la investigación muestras de PVC plastificado comercial en vez de muestras fabricadas en el laboratorio. Este enfoque inusual ha demostrado que es posible para los conservadores encontrar tratamientos de limpieza específicos para obras de arte realizadas en materiales plásticos, incluso si la composición del plástico es desconocida. Por lo tanto, la metodología propuesta en esta investigación abre un nuevo camino para hacer frente a la limpieza de los objetos plásticos en los museos y centros de conservación, ya que la composición de estos objetos en las colecciones

de arte no es siempre conocida, lo que dificulta a los conservadores encontrar métodos de limpieza adecuados.

Por otra parte, siguiendo la metodología de estudio propuesta inicialmente, los métodos de limpieza descubiertos durante la investigación sobre muestras de PVC plastificados comerciales fueron probados en un verdadero objeto de PVC plastificado (una cabeza de muñeca antigua) con signos de degradación. Mediante este "proceso iterativo", varios métodos de limpieza seguros y eficientes fueron encontraron, lo que demostró la idoneidad de la metodología.

Metodología propuesta para la investigation de la limpieza obras de arte compuestas de PVC plastificado:



13.3.2. Investigación de los resultados de la limpieza en seco.

- El PVC plastificado resultó sensible tanto a las características químicas del agente de limpieza como al tiempo de ejecución de la limpieza;

- Agentes limpiadores en seco (tejidos) con igual composición química produjeron similares alteraciones físicas y químicas en el PVC (plastificado y no plastificado);

- Los agentes de limpieza compuestos de fibras de poliamida interactuaron con el plastificante del PVC en limpiezas breves o prolongadas, así como la limpieza por medio de hisopos de algodón causó daños a las muestras de PVC debido a la migración del plastificante. Por tanto, los agentes de limpieza en seco compuestos de fibras de algodón o poliamida no son recomendables para la limpieza de PVC plastificado;

- Limpiezas en seco mediante limpiadores en seco compuestos de fibras de poliamida-poliéster no produjeron cambios físicos ni químicos en el PVC plastificado utilizado en esta investigación, cuando fueron utilizados en tiempos de limpieza breves. Sin embargo, se produjo migración del plastificante después de utilizarse en tiempos de limpieza largos. Por lo tanto, agentes de limpieza en seco compuestos de poliamida-poliéster, son recomendables para el PVC plastificado siempre que se realicen pruebas previas de control;

- La relación entre las bandas FTIR 739 cm^{-1} plastificante/635 cm^{-1} PVC polímero, resultaron ser un indicador de la migración del plastificante del PVC debido a la limpieza con agentes de limpieza en seco: cuanto mayor es el cociente, mayor es la migración de plastificante con la limpieza;

- Cambios en la relación entre las bandas FTIR PVC cristalino (634 cm^{-1})/ PVC amorfo (612 cm^{-1}) han resultado ser un indicador adecuado de las modificaciones del polímero de PVC producidas por métodos de limpieza en seco;

- Desde un punto de vista de la eficiencia, los limpiadores comerciales en seco compuestos de fibras de poliéster-poliamida resultaron los más eficientes para la limpieza en seco de las superficies de PVC plastificado investigados en este estudio, en comparación a los hisopos de algodón y agentes en secos compuestos de fibras de poliamida;

- La relación directa entre la eficiencia y la textura de los agentes limpiadores en seco (tejidos) no pudo establecerse en la presente investigación.

13.3.3. Investigación de los resultados de la limpieza en húmedo.

- La morfología del PVC plastificado resultó sensible tanto a la naturaleza química como a la concentración de los agentes de limpieza;

- Los disolventes orgánicos utilizados en estado puro causaron modificaciones morfológicas del PVC plastificado;

- Ni el agua desionizada ni la disolución básica acuosa de KOH 1M causaron alteraciones físicas o químicas en el PVC plastificado. Sin embargo, la limpieza con disoluciones acuosas de KOH 1M podrían resultar difíciles de controlar y causar limpiezas excesivas, por lo que su uso no es recomendable par la limpieza de obras de arte. Para evitar esto, la concentración de la disolución de KOH debe ser cuidadosamente seleccionada;

- Contrariamente a lo que aparece publicado en la referencias bibliográficas, uno de los detergentes utilizados en esta investigación resultó extraer

plastificante de las muestras de PVC cuando fue utilizado durante tiempos de limpieza largos, a pesar del hecho de que había sido recomendado para la limpieza de obras de arte realizadas de plásticos. Por tanto, a pesar de que las soluciones de detergentes puedan utilizarse eficazmente para limpieza de plásticos, éstas deben ser probados antes de ser aplicadas en PVC plastificado para evitar la extracción de plastificante;

- El limpiador comercial formulado específicamente para la limpieza de plásticos en conservación de arte, no produjo una mejor respuesta en términos de seguridad y eficiencia con respecto a los agentes limpiadores de composición conocida. A su vez, resultó dejar residuos después de su uso en superficies rugosas de PVC plastificado. Dado los resultados obtenidos, es recomendable probar cualquier producto de limpieza comercial antes de su uso para la limpieza de PVC plastificado;

- El "Índice de Plastificante" (IP) (Ec.1) propuesto y desarrollado en esta investigación ha resultado ser una herramienta adecuada no sólo para la investigación de la migración del plastificante durante los tratamientos de limpieza en húmedo, sino también para la selección de proporciones y tiempos de limpieza adecuados en disoluciones limpiadoras compuestas por varios disolventes.

$$\text{(Ec.1) } \mathbf{IP}\ (\%) = \left(\frac{\left(\frac{A_{1722\ cm^{-1}}}{A_{1426\ cm^{-1}}}\right)_{después\ de\ la\ limpieza} - \left(\frac{A_{1722\ cm^{-1}}}{A_{1426\ cm^{-1}}}\right)_{antes\ de\ la\ limpieza}}{\left(\frac{A_{1722\ cm^{-1}}}{A_{1426\ cm^{-1}}}\right)_{antes\ de\ la\ limpieza}} \right) \times 100$$

Por tanto, el IP puede ser considerado como un método alternativo a los parámetros de Hildebrand tradicionalmente utilizados para estimar el grado de interacción entre los materiales y su solubilidad. Además, el "Índice de Plastificante" presenta un gran potencial en la búsqueda de mezclas de

disolventes orgánicos adecuadas para la limpieza de plásticos, debido al hecho de que tanto la suciedad, como los productos de degradación o incluso los residuos de restauraciones antiguas son en muchos casos insolubles en agua o en detergentes, y solo son eliminables mediante disolventes orgánicos;

- Soluciones básicas de KOH y detergentes resultaron ser las disoluciones limpiadoras más efectivas en la eliminación de la suciedad incrustada en PVC plastificado, mientras que los detergentes fueron los agentes de limpieza más adecuados para los productos de degradación en muestras de PVC plastificados envejecidas artificialmente.

A partir de los resultados obtenidos en la presente investigación tras la aplicación de diferentes métodos de limpieza en seco y húmedo sobre superficies PVC plastificado en condiciones normales, degradadas y sucias, puede concluirse que:

1) Los métodos de limpieza de PVC no sólo deben ser adecuados para la composición química del material, sino que también deben tener en cuanta la topografía de la superficie, su estado de degradación y su estado de limpieza, ya que estos factores son críticos en la respuesta del material a la limpieza;

2) Es absolutamente necesario probar cualquier producto de limpieza antes de su uso en PVC plastificado, ya que pueden producirse resultados adversos desde el punto de vista químico, físico y topográfico.

13.3.4. Cuantificación y evaluación de los métodos de limpieza.

Un nuevo método para la cuantificación de la eficiencia de la limpieza en los materiales plásticos se ha encontrado sobre la base de la propuesta de un "Índice de Eficiencia de limpieza ", que se puede determinar tanto mediante parámetros

espectrocolorimétricos (parámetro L * o luminosidad en el espacio de color CIElab) (Ec.2) como mediante parámetros profilométricos (parámetro Sq o desviación estándar de la amplitudes de la superficie de área medida) (Ec.3) :

(Ec.2) $$\text{Eficiencia de Limpieza } (\%) = \left(\frac{L^*_{limpiada} - L^*_{sucia}}{L^*_{sin\,manchar} - L^*_{sucia}}\right) \times 100$$

(Ec.3) $$\text{Eficiencia de Limpieza } (\%) = \left(\frac{Sq_{limpiada} - Sq_{sucia}}{Sq_{\text{sin}\,manchar} - Sq_{sucia}}\right) \times 100$$

Cuanto mayor es el valor del Índice de Eficiencia de limpieza, mayor es la eficiente de la limpieza. Mediante la aplicación de estas ecuaciones es posible comparar varios métodos de limpieza y determinar su eficacia, lo que puede ayudar a conservadores a decidir los métodos de limpieza más eficientes para sus casos particulares. Comparando ambos índices, se puede afirmar que la eficiencia de la limpieza calculada por métodos profilométricos muestra algunas ventajas sobre los cálculos basados en espectrocolorimetría. Estas ventajas se refieren a la versatilidad de la técnica profilométrica, que puede utilizarse en cualquier tipo de superficie, sin tener en cuenta el tamaño del objeto, el volumen o la topografía. Asimismo, contrariamente a colorimetría, donde el dispositivo de medición debe estar en contacto con el objeto, la profilometría es una técnica que puede utilizarse sin establecer contacto con la superficie a analizar, así como la cuantificación mediante colorimetría depende del contraste entre la suciedad y el sustrato, lo que es en si mismo una desventaja con respecto a las técnicas profilométricas. Por el contrario, la colorimetría es una técnica más económica y fácil de utilizar en comparación con profilometría, lo que la hace más asequible para los centro de conservación y de investigación.

En cuanto a las técnicas microscópicas utilizadas en esta investigación para el examen de los métodos de limpieza, la microscopía óptica ha resultado una técnica de utilizad en la obtención de información complementaria a las técnicas de cuantificación, tales como colorimetría o la profilometría. Por medio de la microscopía

óptica, es posible obtener una primera evaluación de la eficacia de la limpieza, incluso para materiales en estado degradado o sucio, proporcionando información valiosa para la valoración de la limpieza en museos. Contrariamente a las técnicas microscópicas, tales como la microscopía óptica o microscopía electrónica de barrido, las técnicas profilométricas no sólo ofrecen imágenes en 2D y 3D, sino que también ofrecen perfiles de rugosidad de la superficie. Así mismo, las imágenes en 3D obtenidas mediante profilometría se encuentran dentro de la escala milimétrica, mientras que mediante microscopía SEM solo pueden lograrse imágenes a escala sub-micrométrica. El hecho de que las técnicas profilométricas no necesiten ningún muestreo (al contrario de SEM) o contacto con la superficie examinada, hace que sean adecuadas para el examen de los efectos de la limpieza en museos. Conjuntamente, las imágenes en 3D y parámetros de rugosidad proporcionados constituyen una herramienta importante para evaluar los cambios topográficos de las superficies de plástico durante la limpieza, así como proporcionan un método alternativo a los análisis químicos (ATR-FTIR) para la detección de residuos dejados por los agentes de limpieza sobre las superficies limpiadas. Por último, cabe destacar que las técnicas profilométricas también han demostrado ser una técnica adicional para la evaluación de la intensidad y la homogeneidad del proceso de limpieza mediante los perfiles de rugosidad y las imágenes en 3D, suponiendo una valiosa ayuda para los conservadores.

Por otra parte, la técnica ATR-FTIR ha sido utilizada en esta investigación para la recopilación de información cualitativa y cuantitativa de los métodos de limpieza en seco y en húmedo sobre PVC comercial y no comercial. La información cualitativa proporcionada por ATR-FTIR a lo largo de los experimentos de limpieza puede resumirse en:

- Identificación química del PVC polímero y sus plastificantes,
- identificación química de los compuestos que forman la suciedad depositada,
- identificación química de la composición de los agentes de limpieza en seco,
- identificación química de los residuos dejados por los agentes limpiadores sobre la superficie de las muestras de PVC,

- identificación de las bandas correspondientes a los grupos funcionales de la suciedad antes y después de la limpieza, pudiendo ser utilizadas para la evaluación cualitativa de la eficacia de la limpieza,
- identificación de las modificaciones químicas y físicas del PVC como consecuencia de la limpieza,
- investigación de las alteraciones de la cristalinidad del PVC como consecuencia de la limpieza, mediante la relación de intensidad de la banda C–Cl cristalina y amorfa del PVC: A634/ A612,
- investigación de la migración del plastificante desde el polímero de PVC como consecuencia de la limpieza, mediante la relación de intensidad de la banda C-H del plastificante y la banda C-Cl del PVC: A739 / A635.

Información cuantitativa de los efectos de la limpieza fue obtenida mediante el "Índice de plastificante" (Eq.1) mencionado en la sección 5.3. Esta ecuación se basa en la relación de las intensidades de los picos de la banda de carbonilo del plastificante y la banda de C-H del polímero de PVC antes y después de los tratamientos de limpieza $\left(\frac{A_{1722\ cm^{-1}}}{A_{1426\ cm^{-1}}}\right)$. La disminución del Índice de plastificante (expresado en%) representa la pérdida de plastificante en el polímero de PVC debido a la acción de limpieza.

Por otra parte, dado que la técnica ATR- FTIR es una técnica de análisis de superficie, no pudieron evaluarse los efectos de la limpieza en el interior del PVC, tales como la extracción de plastificante o la penetración de los agentes de limpieza en el polímero. Del mismo modo, no pudieron detectarse variaciones de peso cuando las muestras fueron pesadas después de la limpieza, dado que las limpiezas realizadas fueron realizadas en la superficie y durante tiempos cortos. Variaciones de peso solo pudieron detectarse después de la inmersión de las muestras de PVC en los disolventes de limpieza, debido a la extracción de cantidades medibles de plastificante.

13.3.5. Productos de degradación y limpieza

Las técnicas espectroscópicas (ATR-FTIR) y cromatográficas (GC-MS y LC-MS) han resultado ser eficaces en la investigación e identificación de los productos generados en los objetos de PVC plastificado, como consecuencia de su degradación o envejecimiento. La información aportada por estas técnicas permite una mejor comprensión de la degradación química del PVC, ayudando a conservadores a encontrar métodos de limpieza adecuados y específicos de acuerdo con el estado de degradación del PVC. Sin embargo, existen diferencias significativas entre las dos técnicas que deben ser tenidas en cuenta cuando se trabaja en museos. En el caso de la espectroscopía ATR-FTIR, la penetración de esta técnica es solamente de algunas micras, así como no requiere ninguna preparación de las muestras para su análisis. Estas características hacen de la espectroscopía ATR-FTIR una técnica adecuado para la investigación del proceso de limpieza en la superficie de cualquier material de PVC en museos y colecciones de arte. Sin embargo, en aquellos casos en los que se requiere una identificación más profunda de los efectos causados en el material por la limpieza o de la composición de los productos de degradación, la espectroscopia ATR-FTIR resulta insuficiente. En estos casos, deben utilizarse técnicas cromatográficas, aun si bien necesitan muestras del material a analizar. Por otro lado, la técnica analítica de espectroscopía fotoelectrónica de rayos-X (XPS) utilizada en esta investigación, ha proporcionado información valiosa sobre la composición elemental del material, contribuyendo a la identificación de los aditivos en el PVC. Sin embargo, esta técnica no es recomendable para el estudio de PVC plastificado, debido a los daños que la evaporación de plastificante puede producir dentro del equipo XPS, debido a la presión de vapor relativamente alta de los plastificantes. Del mismo modo, los cambios físicos en el material de PVC debido a las reacciones de foto-envejecimiento han sido investigados con éxito mediante colorimetría, medición del brillo y espectroscopia UV-Vis. Todas estas técnicas han proporcionado información complementaria al análisis químico, ayudando a entender la velocidad del proceso de degradación mediante la monitorización del color, del brillo y de la formación de "grupos cromóforos" en el material de PVC plastificado.

Respecto a la degradación del PVC plastificado comercial, se detectó la formación de enlaces conjugados C=C en el polímero de PVC como consecuencia de un proceso típico de deshidrocloración, dando lugar a una coloración amarillenta del mismo. También se detectó la degradación del plastificante principal (DINP), que dio lugar a la formación de alcoholes C9 y anhídrido ftálico a través de una reacción Norrish II. Sin embargo, mediante métodos cualitativos y cuantitativos se demostró que la degradación del material no fue lineal en el tiempo. El proceso de envejecimiento fue particularmente lento durante la primera y segunda semana, a partir de la cual el incremento de la foto-degradación fue considerable. Este cambio de la cinética de degradación se debió a la disminución progresiva de la eficacia de los estabilizadores UV identificados en el polímero, produciendo alteraciones químicas y físicas, tales como el cambio de color y la pérdida de brillo. Finalmente, el proceso de foto-envejecimiento artificial condujo a la formación de una capa de productos de degradación en la superficie del polímero que fue visible a simple vista. Por el contrario, la degradación de la muñeca de PVC plastificado no fue debida al envejecimiento homogéneo de la superficie, sino a la migración de lubricantes internos en áreas específicas de la misma. Los productos de degradación identificados fueron: bis (2-etil-hexilo) ftalato, confirmando que el plastificante ftalato en la muñeca no sufrió degradación como en el caso del PVC comercial. Por lo tanto, las vías de degradación fueron diferentes en ambos materiales de PVC plastificado.

Desde el punto de vista de la conservación de arte, el presente trabajo ha demostrado la importancia que la correcta identificación de los productos de degradación tiene en la selección de los métodos de limpieza de los productos de envejecimiento y degradación de los materiales de PVC. A su vez, dado que la velocidad a la que los productos de degradación se forman depende de cada fase del proceso de degradación, la etapa de degradación en la que se encuentra el PVC plastificado también debe ser considerada a la hora de elegir el método de limpieza apropiado. Como resultado de esta investigación, los métodos de limpieza en seco resultaron ineficaces en la eliminación de productos de degradación y aditivos

migrados a la superficie, mientras que los métodos de limpieza en húmedo produjeron una mejor y más homogénea eliminación de los mismos.

13.4. Investigaciones futuras.

Debe tenerse en cuenta que sería aconsejable la realización de investigaciones futuras con respecto al comportamiento del material después de la limpieza. De esta manera, el seguimiento de la limpieza con el tiempo podría proporcionar datos valiosos para los conservadores, tales como:

a) el tiempo que transcurre hasta que una nueva limpieza, es necesaria,

b) información sobre las consecuencias adversas debido a los tratamientos de limpieza,

c) información sobre las consecuencias debido a la eliminación de productos de degradación de la superficie de plástico.

A pesar de que la contribución del presente estudio se limita al PVC, el propósito para futuros estudios tiene como objetivo el establecimiento de métodos adecuados, eficaces y de aplicación común para la limpieza y conservación de objetos de plástico que forman parte de nuestro patrimonio cultural. Para ello, el siguiente paso sería la aplicación a otros plásticos de interés en el entorno del museo, tales como poliésteres, poliuretano o poli (metacrilato de metilo) (PMMA), de la metodología desarrollada en esta investigación.